AUTHENTICATED
U.S. GOVERNMENT
INFORMATION
GPO

FEDERAL REGISTER

Vol. 80 Thursday,
No. 33 February 19, 2015

Part II

Environmental Protection Agency

40 CFR Part 136
Clean Water Act Methods Update Rule for the Analysis of Effluent; Proposed Rule

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 136

[EPA–HQ–OW–2014–0797; FRL–9920–55–OW]

RIN 2040–AF48

Clean Water Act Methods Update Rule for the Analysis of Effluent

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed rule.

SUMMARY: EPA proposes changes to pollutant analysis methods that are used by industries and municipalities to analyze the chemical, physical, and biological components of wastewater and other environmental samples that are required by regulations under the Clean Water Act. EPA designed the proposed changes to increase flexibility for the regulated community, improve data quality, and update CWA methods to keep current with technology advances and analytical methods science. EPA updates and revises the CWA analytical methods from time to time, the most recent updates being completed in 2012. The new set of proposed changes described in this notice include revisions to current EPA methods and new and/or revised methods published by voluntary consensus standard bodies, such as ASTM International and the Standard Methods Committee. EPA also proposes to approve certain methods reviewed under the alternate test procedures program and clarify the procedures for EPA approval of nationwide and limited use alternate test procedures. Further, EPA proposes amendments to the procedure for determination of the method detection limit to address laboratory contamination and to better account for intra-laboratory variability.

DATES: Comments on this proposed rule must be received on or before April 20, 2015.

ADDRESSES: Submit your comments, identified by Docket ID No. EPA–HQ–OW–2014–0797, by one of the following methods:

- *www.regulations.gov:* Follow the on-line instructions for submitting comments.
- *Email: OW-Docket@epa.gov,* Attention Docket ID number EPA–HQ–OW–2014–0797.
- *Mail:* Water Docket, Environmental Protection Agency, Mail code: 4203M, 1200 Pennsylvania Ave. NW., Washington, DC 20460. Attention Docket ID number EPA–HQ–OW–2014–0797. Please include a total of 3 copies.
- *Hand Delivery:* Water Docket, EPA Docket Center, EPA West Building, Room 3334, 1301 Constitution Ave. NW., Washington, DC, Attention Docket ID number EPA–HQ–OW–2014–0797. Such deliveries are only accepted during the Docket's normal hours of operation, and special arrangements should be made for deliveries of boxed information by calling 202–566–2426.

Instructions: Direct your comments to Docket ID number EPA–HQ–OW–2014–0797. EPA's policy is that all comments received will be included in the public docket without change and may be made available online at *www.regulations.gov,* including any personal information provided, unless the comment includes information claimed to be Confidential Business Information (CBI) or other information whose disclosure is restricted by statute. Do not submit information that you consider to be CBI or otherwise protected through *www.regulations.gov* or email. The *www.regulations.gov* Web site is an ''anonymous access'' system, which means EPA will not know your identity or contact information unless you provide it in the body of your comment. If you send an email comment directly to EPA without going through *www.regulations.gov* your email address will be automatically captured and included as part of the comment that is placed in the public docket and made available on the Internet. If you submit an electronic comment, EPA recommends that you include your name and other contact information in the body of your comment and with any disk or CD–ROM you submit. If EPA cannot read your comment due to technical difficulties and cannot contact you for clarification, EPA may not be able to consider your comment. Electronic files should avoid the use of special characters, any form of encryption, and be free of any defects or viruses.

Docket: All documents in the docket are listed in the *www.regulations.gov* index. Although listed in the index, some information in the docket is not publicly available, *e.g.,* CBI or other information whose disclosure is restricted by statute. Certain other material, such as copyrighted material, will be publicly available only in hard copy. Publicly available docket materials are available either electronically in *www.regulations.gov* or in hard copy at the Water Docket in EPA Docket Center, EPA/DC, EPA West William J. Clinton Building, Room 3334, 1301 Constitution Ave. NW., Washington, DC. The Public Reading Room is open from 8:30 a.m. to 4:30 p.m., Monday through Friday, excluding legal holidays. The telephone number for the Public Reading Room is 202–566–1744 and the telephone number for the Water Docket is 202–566–2426.

FOR FURTHER INFORMATION CONTACT: Adrian Hanley, Engineering and Analysis Division (4303T), Office of Water, Environmental Protection Agency, 1200 Pennsylvania Ave. NW., Washington, DC 20460–0001; telephone: 202–564–1564; email: *hanley.adrian@epa.gov.*

SUPPLEMENTARY INFORMATION:

Table of Contents

I. General Information
II. Overview
III. Statutory Authority
IV. Purpose and Summary of Proposed Rule
V. Statutory and Executive Order Reviews

I. General Information

A. Does this Action apply to me?

Entities potentially affected by the requirements of this proposed action include:

Category	Examples of potentially affected entities
State, Territorial, and Indian Tribal Governments.	States, territories, and tribes authorized to administer the National Pollutant Discharge Elimination System (NPDES) permitting program; states, territories, and tribes providing certification under CWA section 401; state, territorial, and tribal owned facilities that must conduct monitoring to comply with NPDES permits.
Industry	Facilities that must conduct monitoring to comply with NPDES permits.
Municipalities	Publicly Owned Treatment Works (POTWs) or other municipality owned facilities that must conduct monitoring to comply with NPDES permits.

This table is not exhaustive, but rather provides a guide for readers regarding entities likely to be affected by this action. This table lists types of entities that EPA is now aware of that could potentially be affected by this action. Other types of entities not listed in the table could also be affected. To determine whether your facility is affected by this action, you should carefully examine the applicability language at 40 CFR 122.1 (NPDES purpose and scope), 40 CFR 136.1 (NPDES permits and CWA) and 40 CFR 403.1 (pretreatment standards purpose and applicability). If you have questions regarding the applicability of this action to a particular entity, consult the appropriate person listed in the preceding **FOR FURTHER INFORMATION CONTACT** section.

B. What should I consider as I prepare my comments for EPA?

1. Submitting CBI. Do not submit CBI to EPA through *www.regulations.gov* or email. Clearly mark the part or all of the information that you claim to be CBI. For CBI information in a disk that you mail to EPA, mark the outside of the disk as CBI and then identify electronically within the disk the specific information that is claimed as CBI. In addition to one complete version of the comment that includes information claimed as CBI, a copy of the comment that does not contain the information claimed as CBI must be submitted for inclusion in the public docket. Information so marked will not be disclosed except in accordance with procedures for handling and protection of CBI set forth in 40 CFR part 2.

2. Tips for Preparing Your Comments. When submitting comments, remember to:

- Identify the rulemaking by Docket ID number and other identifying information (subject heading, **Federal Register** date and page number).
- Explain why you agree or disagree, suggest alternatives, and substitute language for your requested changes.
- Describe any assumptions and provide any technical information and/or data that you used.
- If you estimate potential costs or burdens, explain how you arrived at your estimate in sufficient detail to allow for it to be reproduced.
- Provide specific examples to illustrate your concerns, and suggest alternatives.
- Explain your views as clearly as possible, avoiding the use of profanity or personal threats.
- Make sure to submit your comments by the comment period deadline identified.

II. Overview

This preamble describes the reasons for the proposed rule; the legal authority for the proposed rule; a summary of the proposed changes and clarifications; and explanation of the abbreviations and acronyms used in this document. In addition, this preamble solicits comment and data from the public.

Abbreviations and Acronyms Used in the Preamble and Proposed Rule Text

AA: Atomic Absorption
ADMI: American Dye Manufacturers Institute
ASTM: ASTM International
ATP: Alternate Test Procedure
CAS: Chemical Abstract Services
CFR: Code of Federal Regulations
CWA: Clean Water Act
EPA: Environmental Protection Agency
FLAA: Flame Atomic Absorption Spectroscopy
GC: Gas Chromatograph
ICP/AES: Inductively Coupled Plasma—Atomic Emission Spectroscopy
ICP/MS: Inductively Coupled Plasma—Mass Spectrometry
LCS: Laboratory Control Sample
MS: Mass Spectrometry
MS/MSD: Matrix Spike/Matrix Spike Duplicate
NPDES: National Pollutant Discharge Elimination System
POTW: Publicly Owned Treatment Works
QA: Quality Assurance
QC: Quality Control
SM: Standard Methods
STGFAA: Stabilized Temperature Graphite Furnace Atomic Absorption Spectroscopy
USGS: United States Geological Survey
VCSB: Voluntary Consensus Standards Body

III. Statutory Authority

EPA proposes this regulation under the authorities of sections 301(a), 304(h), and 501(a) of the CWA, 33 U.S.C. 1311(a), 1314(h), and 1361(a). Section 301(a) of the CWA prohibits the discharge of any pollutant into navigable waters unless the discharge complies with, among other provisions, a NPDES permit issued under section 402 of the CWA. Section 304(h) of the CWA requires the Administrator of the EPA to ''. . . promulgate guidelines establishing test procedures for the analysis of pollutants that shall include the factors which must be provided in any certification pursuant to [section 401 of the CWA] or permit application pursuant to [section 402 of the CWA].'' Section 501(a) of the CWA authorizes the Administrator to ''. . . prescribe such regulations as are necessary to carry out this function under [the CWA].'' EPA generally has codified its test procedure regulations (including analysis and sampling requirements) for CWA programs at 40 CFR part 136, though some requirements are codified in other parts (*e.g.,* 40 CFR Chapter I, Subchapters N and O).

IV. Purpose and Summary of Proposed Rule

The CWA requires EPA to promulgate test procedures (analytical methods) for analyses required in NPDES permit applications and for reports required under NPDES permits. EPA codifies these approved test procedures at 40 CFR part 136. EPA regions, as well as authorized states, territories and tribes issue NPDES permits. These permits must include conditions designed to ensure compliance with the technology-based and water quality-based requirements of the CWA, including in many cases, restrictions on the quantity of specific pollutants that can be discharged as well as pollutant measurement and reporting requirements. Often, entities have a choice in deciding which approved test procedure they will use for a specific pollutant because EPA has approved the use of more than one.[1]

The procedures for the analysis of pollutants required by CWA section 304(h) are a central element of the NPDES permit program. Examples of where these EPA analytical methods must be used include, among others, the following: (1) Applications for NPDES permits, (2) sampling or other reports required under NPDES permits, (3) other requests for quantitative or qualitative effluent data under the NPDES regulations, (4) State CWA 401 certifications and (5) sampling and analysis required under EPA's General Pre-Treatment Regulations for Existing and New Sources of Pollution 40 CFR 136.1 and 40 CFR 403.12(b)(5)(v).

Periodically, EPA proposes to update the approved methods in 40 CFR part 136. In general, the changes in this proposed action fall into the following categories: new and revised EPA methods and new and revised methods adopted by VCSBs; methods EPA has reviewed under EPA's national alternate test procedures (ATP) program and preliminarily concluded are appropriate for nationwide use; certain corrections to 40 CFR part 136; and amendments to the procedure for determination of the MDL primarily to address laboratory contamination and to better account for intra-laboratory variability. Collectively, EPA's current understanding indicates that adoption of these proposed revisions would improve data quality, update methods to keep current with technology advances, provide additional

[1] NPDES permit regulations also specify that the approved method needs to be sufficiently sensitive. See 40 CFR 122.21.e.3.

clarity for ATPs, and provide the regulated community with greater flexibility.

The following paragraphs provide details on the proposed revisions.

A. Changes to 40 CFR 136.3 and Appendix A to Include New Versions of Previously Approved EPA Methods

EPA proposes revisions to the approved EPA Methods 608, 624, and 625 which it adopted in 1984, and proposes to make a minor correction to the parameter list in EPA Method 611. These four EPA methods are listed in Table IC at 40 CFR part 136. Methods 608 and 625 also are listed in Tables ID and IG, and Methods 624 and 625 are listed in Table IF. EPA also proposes minor corrections to microbiological methods 1600, 1603, 1680, and 1682. These four EPA methods are listed in Table IA at 40 CFR part 136, and Methods 1600 and 1603 are listed in Table IH.

1. Methods 608, 624, and 625

The proposed revisions take advantage of improvements in analytical technology and allow greater flexibility in order to accommodate future improvements to the methods and generally obviate any need for additional revisions. EPA revised these methods in collaboration with other EPA offices, states, and environmental laboratory organizations. The revisions conform to the following principles:

Updated Technology: EPA changed the GC columns from packed columns to capillary (open tubular) columns. Capillary columns provide greater resolution and decreased adsorption (loss) of the analytes and, therefore, result in a significant improvement in the accuracy (recovery) and precision of the results.

Method Flexibility: The revised methods allow greater method flexibility so that the methods more closely align with 40 CFR 136.6. This flexibility would make it easier for laboratories to make in-house improvements and technology updates in the future that will not compromise the original quality control acceptance criteria of the methods. Consistent with 40 CFR 136.6, EPA built into the methods procedures that will allow a laboratory to make limited changes to a method without applying for an ATP; however, the laboratory must document that the revisions produce results consistent with the QC acceptance criteria in the method in order to take advantage of the built-in flexibility. For example, the revised methods allow access to a greater list of compounds than the list of compounds determined by the original versions of these methods, provided that the laboratory can demonstrate acceptable accuracy and precision with these analytes in the specified matrices. The expanded list of compounds is an amalgamation of lists from Methods 1624, 1625, 1699 and other EPA methods that demonstrate the technology can be used to quantify these additional analytes. The revisions also allow more flexibility to adopt different extraction procedures, such as solid phase extraction. The revised methods include requirements for a laboratory to develop its own in-house QC acceptance criteria for tests of the laboratory control sample and tests of matrix spike and matrix spike duplicate samples, provided the LCS and MS/MSD meet minimum criteria specified in the method. The revisions also clarify that hydrogen can be used as a carrier gas for the methods. Some of the flexibility EPA proposes to add to the methods is currently specified in 40 CFR 136.6(b)(4)(xvi). Because EPA proposes to incorporate that flexibility directly into the method, EPA proposes to delete the corresponding text from 40 CFR 136.6.

Method Harmonization: EPA updated these methods to make them more consistent with the most recent updates of similar methods from the Office of Ground Water and Drinking Water and the Office of Resource Conservation and Recovery. EPA revised the required QC frequencies and standards (internal standards and surrogates) to more closely match the methods from other EPA analytical method programs. Laboratories that run methods from multiple EPA programs will benefit from these revisions.

2. Method 611

EPA proposes a minor correction to a parameter name in the parameter list of of EPA Method 611 (''Haloethers''). As currently listed, the compound with the CAS Registry Number 108–60–1 is bis(2-chloroisopropyl)ether. EPA proposes to correct the analyte name to 2,2′-oxybis(1-chloropropane), which matches the CAS Number 108–60–1. The original analyte name bis(2-chloroisopropyl)ether has a CAS number of 39638–32–9. EPA is unaware that this chemical has ever been in industrial production, and is therefore unlikely to be a compound of monitoring concern. Furthermore, it is not possible to procure an analytical standard reference material for the compound with CAS number 39638–32–9. The compound in the parameter list should be 2,2′-oxybis(1-chloropropane), CAS number 108–60–1.

3. Methods 1600, 1603, 1680, and 1682

EPA proposes the following changes for EPA microbiological methods 1600, 1603, 1680, and 1682. These changes correct typographical or other errors that EPA identified in the methods after publication. EPA proposes to revise all of these methods with new EPA document numbers and dates.

a. EPA Method 1600 for Enterococci using membrane filtration: In Table 3 Verification controls, EPA changed the negative control for brain heart infusion broth incubated at 45 °C from *E. coli* to *Enterobacter aerogenes. E. coli* is thermotolerant and *E. aerogenes* is not, so *E. coli* is not an appropriate negative control when heated.

b. EPA Method 1603 for *E. coli* using membrane filtration: In Section 11.5, EPA changed the number of colonies on a countable plate from 20–60 to 20–80 colonies. Sixty colonies was a typographical error. In addition the following sentence was inadvertently omitted and EPA included it: Sample volumes of 1–100 mL are normally tested at half-log intervals (*e.g.,* 100, 30, 10, and 3 mL).

c. EPA Method 1680 for fecal coliforms using multiple tube fermentation: in Section 3.1 Definitions, the sentence ''The predominant fecal coliform is *E. coli.''* should read ''The predominant fecal coliform can be *E. coli.''*

d. EPA Method 1682 for *Salmonella* by MSRV medium: (1) In Section 9.3, Table 2, the lab-prepared spike acceptance criteria should read ''Detect—254%'' and ''Detect—287%'' and (2) in Section 14.5, Table 9, the spiked *Salmonella* for Example 2, Liquid should read ''3.7×10^{8} CFU/mL.''

B. Methods Incorporated by Reference

Currently, hundreds of methods and ATPs are incorporated by reference within 40 CFR part 136. In most cases, 40 CFR part 136 contains multiple approved methods for a single pollutant and regulated entities often have a choice in the selected method. The proposed rule contains revisions to methods that will be incorporated by reference from two VCSBs: Standard Methods and ASTM. EPA proposed VCSB methods in compliance with the National Technology Transfer Act (see Section V.I below). The proposed VCSB methods are available on their respective VCSB Web sites to everyone at a cost determined by the VCSB, generally from $40 to $80. Both organizations also offer memberships or subscriptions that allow unlimited access to their methods. The cost of obtaining these methods is not a

significant financial burden for a discharger or environmental laboratory, making the methods reasonably available. The proposal also includes USGS methods and vendor ATPs that are incorporated by reference. The ATPs and USGS methods are available free of charge on the Web site for that organization. Therefore, EPA concludes that the proposed methods and ATPs incorporated by reference are reasonably available. The individual standards are discussed in greater detail below.

C. Changes to 40 CFR 136.3 to Include New Versions of Approved Standard Methods

EPA proposes to approve new versions of currently approved Standard Methods. The new versions of currently approved Standard Methods clarify or improve the instructions in the method, improve the QC instructions, or make editorial corrections. Consistent with the previous method update rule (77 FR 29767–29768), EPA proposes to generally approve and include in 40 CFR part 136 only the most recent version of a method published by the Standard Methods Committee by listing only one version of the method with the year of publication designated by the last four digits in the method number (*e.g.,* SM 3111 B–2011). The date indicates the latest revision date of the method. This allows use of a specific method in any edition that includes a method with the same method number and year of publication.

Most of the revisions that EPA proposes to Standard Methods previously approved in 40 CFR part 136 do not contain any substantive changes. The following describes the proposed non-substantive changes related to Standard Methods in 40 CFR part 136. Each entry contains the proposed Standard Methods number and date, the parameter, and a brief description of the analytical technique. The methods listed below are organized according to the table at 40 CFR part 136 in which they appear.

The following changes would apply to Table IA at 40 CFR part 136:

1. SM 9221 (B,C,E,F)–2006, Coliform (fecal), Coliform (fecal) in presence of chlorine, Coliform (total), Coliform (total) in presence of chlorine, *E. coli,* most probable number (MPN), 5 tube 3 dilution.
2. SM 9223–2004, *E. coli,* multiple tube/multiple well.
3. SM 9230 (B,C)–2007, Fecal Streptococci, Enterococci, most probable number (MPN), 5 tube 3 dilution or membrane filtration.

The following changes would apply to Table IB at 40 CFR part 136:

1. SM 2120 B–2011, color, platinum cobalt method.
2. SM 2130 B–2011, turbidity, nephelometric method.
3. SM 2310 B–2011, acidity, titration using electrometric endpoint or phenolphthalein endpoint.
4. SM 2320 B–2011, alkalinity, electrometric or colorimetric titration to pH 4.5.
5. SM 2340 B–2011 and SM 2340 C–2011, hardness, by the calculation method or EDTA titration.
6. SM 2510 B–2011, conductivity, Wheatstone bridge method.
7. SM 2540 B–2011, SM 2540 C–2011, SM 2540 D–2011, SM 2540 E–2011, and SM 2540 F–2011, total, filterable, non-filterable, volatile, and settleable residue (solids, listed in the same order as the method numbers), all by gravimetric methodologies.
8. SM 2550 B–2010, temperature, thermometric.
9. SM 3111 B–2011, SM 3111 C–2011, SM 3111 D–2011, and SM 3111 E–2011, metals, direct aspiration AA methods with different gas mixtures. Each method has a different list of metals; no changes are proposed to these lists.
10. SM 3112 B–2011, metals, applicable to mercury, cold-vapor atomic absorption spectrometric method.
11. SM 3114 B–2011 and SM 3114 C–2011, total arsenic and total selenium, hydride generation/atomic absorption spectrometric methods. Both analyze total arsenic and total selenium.
12. SM 3120 B–2011, metals, ICP method; no changes are proposed for the approved list of metals.
13. SM 3125 B–2011, metals, ICP/MS method; no changes are proposed for the approved list of metals.
14. SM 3500-Al B–2011, aluminum, colorimetric method.
15. SM 3500-As B–2011, arsenic, colorimetric method (SDDC).
16. SM 3500-Ca B–2011, calcium, titrimetric method (EDTA).
17. SM 3500-Cr B–2011 and SM 3500-Cr C–2011, chromium, the ''B'' method uses a colorimetric method (diphenylcarbazide) and is approved for total or dissolved chromium, the ''C'' method uses ion chromatography and is only approved for dissolved chromium.
18. SM 3500-Cu B–2011 and SM 3500-Cu C–2011, copper, both method sections use colorimetric methods, the ''B'' method uses a neocuproine reagent and the ''C'' method uses a bathocuproine reagent.
19. SM 3500-Fe B–2011, iron, colorimetric method (phenanthroline).
20. SM 3500-K B–2011 and SM 3500–K C–2011, potassium, the ''B'' method is a flame photometric method and the ''C'' method is an electrode method.
21. SM 3500-Mn B–2011, manganese, colorimetric method (persulfate).
22. SM 3500-Na B–2011, sodium, flame photometric method.
23. SM 3500-Pb B–2011, lead, colorimetric method (dithizone).
24. SM 3500-V B–2011, vanadium, colorimetric method (gallic acid).
25. SM 3500-Zn B–2011, zinc, colorimetric method (zincon).
26. SM 4110 (B–D)–2011, anions, ion chromatography; no changes are proposed for the approved analyte list.
27. SM 4140 B–2011, inorganic anions, capillary ion electrophoresis with indirect UV detection: No changes are proposed for the approved analyte list.
28. SM 4500-B B–2011, boron, spectrophotometer or filter photometer (curcumin).
29. SM 4500-Cl^- (B–E)–2011, chloride, titrimetric: (silver nitrate), (mercuric nitrate), automated (ferricyanide), potentiometric titration
30. SM 4500-Cl (B–G)–2011, chlorine (residual), amperometric direct, amperometric direct (low level), iodometric direct, back titration ether end–point, titrimetric: N,N-diethyl-p-phenylenediamine with ferrous ammonium sulfate (DPD-FAS), spectrophotometric (DPD).
31. SM 4500-CN^- (B–G)–2011, cyanide, manual distillation with $MgCl_2$ followed by: Titrimetric, spectrophotometric, manual, ion selective electrode, cyanide amenable to chlorination (CATC); manual distillation with $MgCl_2$, followed by: Titrimetric or spectrophotometric.
32. SM 4500-F^- (B–E)–2011, fluoride, manual distillation, followed by any of the following: Electrode, manual, colorimetric, fluoride dye reagent (SPADNS is the common name for the fluoride dye reagent which is a mixture of chemicals), automated complexone.
33. SM 4500-H^+ B–2011, hydrogen ion (pH), electrometric measurement.
34. SM 4500-NH_3 (B–H)–2011, ammonia (as nitrogen), manual distillation or gas diffusion (pH > 11), followed by any of the following: Titration, electrode, manual phenate, salicylate, or other substituted phenols in Berthelot reaction based methods; automated phenate, salicylate, or other substituted phenols in Berthelot reaction based methods.
35. SM 4500-NO_2^- B–2011, nitrite (as nitrogen), spectrophotometric: Manual.
36. SM 4500-NO_3^- D–2011, nitrate (as nitrogen), ion selective electrode.
37. SM 4500-NO_3^- (E,F, H)–2011, nitrate-nitrite (as nitrogen), colorimetric: Cadmium reduction-manual and automated, and colorimetric: Automated hydrazine.

38. SM 4500-NO_3^- (E,F)–2011, nitrite (as nitrogen), colorimetric: Cadmium reduction-manual and automated.

39. SM 4500-N_{org} (B–D)–2011, total Kjeldahl nitrogen (as nitrogen, organic), semi-automated block digester colorimetric (distillation not required).

40. SM 4500-O (B–G), oxygen (dissolved), Winkler (azide modification), electrode.

41. SM 4500-P (B (5), E–H)–2011, phosphorus and ortho-phosphate, persulfate digestion, digestion, followed by any of the following: Manual or automated ascorbic acid reduction. The ''B Part 5'' method is the persulfate digestion procedure and is required prior to measurement of total phosphorus using SM 4500 P (E–H). The ''E'' through ''G'' methods are approved for both total phosphorus and ortho-phosphate. The ''H'' method is only approved for total phosphorous.

42. SM 4500-S^{2-} (B–D, F,G)–2011, sulfide, sample pretreatment, titrimetric (iodine) analysis, colorimetric (methylene blue), ion selective electrode.

43. SM 4500-SiO_2 (C,E,F)–2011, silica, 0.45-micron filtration followed by any of the following: Colorimetric, manual or automated (Molybdosilicate).

44. SM 4500-SO_3^{2-} B–2011, sulfite, titrimetric (iodine-iodate).

45. SM 4500-SO_4^{2-} (C–G)–2011, sulfate, automated colorimetric, gravimetric, and turbidimetric.

46. SM 5210 B–2011, biochemical oxygen demand (BOD5), dissolved oxygen depletion.

47. SM 5220 (B–D)–2011, chemical oxygen demand (COD), titrimetric; spectrophotometric, manual or automatic.

48. SM 5310 (B-D)–2011, total organic carbon (TOC), combustion, heated persulfate or UV persulfate oxidation.

49. SM 5520 (B,F)–2011, oil and grease, hexane extractable material (HEM): n-hexane extraction and gravimetry, silica gel treated HEM (SGT–HEM): Silica gel treatment and gravimetry.

50. SM 5530 (B,D)–2010, phenols, manual distillation, followed by colorimetric (4AAP) manual.

51. SM 5540 C–2011, surfactants, colorimetric (methylene blue).

The following changes would apply to Table IC at 40 CFR part 136:

1. SM 6200 (B,C)–2011, volatile organic compounds, purge and trap capillary-column gas chromatographic/mass spectrometric (GC/MS), purge and trap capillary-column gas chromatographic (GC).

2. SM 6440 B–2005, polynuclear aromatic hydrocarbons (PAHs), high performance liquid chromatography (HPLC).

The following changes would apply to Table ID at 40 CFR part 136:

1. SM 6630 (B, C)–2007, organochlorine pesticides, gas chromatography (GC).

2. SM 6640 B–2006, acidic herbicide compounds, gas chromatography (GC).

EPA also proposes revisions to certain Standard Methods approved in Part 136 for which Standard Methods adopted updates that contain substantive changes. The following summarizes these changes for each method, organized by the table at 40 CFR part 136 in which they appear.

The following changes would apply to Table IA and/or Table IH at 40 CFR part 136:

1. EPA proposes that the membrane filtration method SM 9222 B–1997 be replaced with SM 9222 B–2006. This method analyzes Coliform (total) in the presence of chlorine. The newer method includes a number of technology updates that do not significantly change the procedure. In addition, the method:

a. Modified the procedure to allow for the use of a humidified incubator if loose-lidded plates are used during incubation.

b. Added a note that five typical and five atypical colonies per membrane need to be identified during coliform verification.

c. Moved the definition of ''Coliform'' that was Section 4 of SM 9222, and renumbered the rest of the document, such that the ''Procedure'' is now Section 4, instead of Section 5. This is not a substantive change except that in Table IA, Parameter 4 ''Coliform (total), in presence of chlorine, number per 100 mL'' the citation for ''MF with enrichment'' would be changed from ''9222 (B+B.5c)–1997'' to ''9222 (B+B.4c)–2006.''

2. EPA proposes that the membrane filtration method SM 9222 D–1997 be replaced with SM 9222 D–2006. This method analyzes Coliform (fecal) and Coliform (fecal) in the presence of chlorine. The new method allows use of a dry recirculating incubator as specified in the culture dishes section. In addition, EPA proposes to add the following footnote to Tables IA and IH regarding SM9222D–2006 for fecal coliform verification frequency: ''The verification frequency is at least five typical and five atypical colonies per sampling site on the day of sample collection & analysis.'' SM 9222 D–2006 specifies that the fecal coliform colonies should be verified ''at a frequency established by the laboratory,'' which can be as low as zero. Colonies need be verified to prevent misidentification of results as false positive or false negative.

3. EPA proposes that the membrane filtration method SM 9222 G–1997 be replaced with SM 9222 G–2006 in Table IH. These methods analyze for *E. coli* and Fecal Coliforms. The newer method includes a number of technology updates that do not significantly change the procedure. In addition, the method now has a modified composition of EC broth to include different quantities of KH_2PO_4 and 4-methylumbelliferyl-β-D-glucuronide.

The following changes would apply to Table IB at 40 CFR part 136:

EPA proposes SM 2120 F–2011 be added to Table IB for Color. EPA previously approved it as SM 2120 E–1993. It is also similar to the currently approved National Council for Air and Stream Improvement, Inc. method that uses American Dye Manufacturers Institute weighted–ordinate spectrophotometric parameters.

1. EPA proposes that SM 3113 B–2004, a metals atomic absorption furnace method, be replaced with the revised version SM 3113 B–2010. The only substantive change would be a reduction in the required replicate analyses of each calibration standard from three to two. Similar EPA methods do not require replicates of each calibration standard.

Finally, Standard Methods requested that EPA propose SM 6810 for the analysis of pharmaceutical and personal care products in water. EPA does not propose to add this method because no supporting data were received by the deadline to demonstrate that the method had undergone full inter-laboratory validation.

D. Changes to 40 CFR 136.3 to Include New Versions of Approved ASTM Methods

EPA proposes to approve new versions of currently approved ASTM methods, for the same reasons outlined in the first paragraph of Section IV.B above. Many of the changes EPA proposes to ASTM Methods approved in 40 CFR part 136 do not contain any substantive changes. The following describes the proposed changes related to ASTM Methods in 40 CFR part 136. Each entry contains (in the following order): proposed ASTM method number and date, the parameter, a brief description of the analytical technique, and a brief description of any substantive changes in this revision from the last approved version of the method. The methods listed below are organized according to the table at 40 CFR part 136 in which they appear.

The following changes would apply to Table IB at 40 CFR part 136:

1. ASTM D 511–09 (A, B), calcium and magnesium, titrimetric (EDTA), AA direct aspiration; the modified method includes less specific calibration requirements for the part A titrimetric method than the previous version. However, the revised requirements are still more comprehensive than other approved methods. Therefore, EPA considers this revised method has adequate calibration criteria.

2. ASTM D 516–11, sulfate ion, turbidimetric, no substantive changes.

3. ASTM D 858–12 (A–C), manganese, atomic absorption (AA) direct aspiration, AA furnace; the modified method allows for pH adjustments in the laboratory, if the sample is returned within 14 days following sampling. The modified method also allows the use of block digestion systems for trace metal analysis, and quality control procedures now require the lab to analyze a continuing calibration blank and continuing calibration verification at a frequency of 10%.

4. ASTM D 859–10, silica, colorimetric, manual; the modified method allows the use of direct reading spectrophotometer or filter photometer, which is common for most approved colorimetric methods.

5. ASTM D 1067–11, acidity or alkalinity, electrometric endpoint or phenolphthalein endpoint; electrometric or colorimetric titration to pH 4.5, manual; no substantive changes

6. ASTM D 1068–10 (A–C), iron, AA direct aspiration; AA furnace; Colorimetric (Phenanthroline); EPA originally approved Parts A–D, but ASTM discontinued Part B. EPA proposes that Parts C and D in the existing 40 CFR part 136 Table 1B, be shifted to Parts B and C to account for the discontinued Part B. Additionally, ASTM increased the frequency of quality control parameters for Test Method A—Atomic Absorption. The method now includes a method blank, a matrix spike sample and a control sample with every ten samples.

7. ASTM D 1126–12, hardness, titrimetric (EDTA); no substantive changes.

8. ASTM D 1179–10, fluoride ion, electrode, manual; colorimetric, (SPADNS); The revision removed calculation, precision and bias, and quality control procedures (method blank, matrix spike, LCS) previously included for Test Method B–Ion Selective Electrode. The method replaces those requirements with a lab duplicate and a reference sample analysis. This is similar to EPA approved SM 4500–F^- (C, D) currently in 40 CFR part 136. The revision also removed the silver sulfate reagent used to remove chloride from the sample, as it is no longer considered a major interference.

9. ASTM D 1246–10, bromide ion, electrode; no substantive changes.

10. ASTM D 1687–12 (A–C), chromium (total) and dissolved hexavalent chromium, colorimetric (diphenyl-carbazide); AA direct aspiration; AA furnace; ASTM modified the method to allow the use of block digestion systems for trace metal analysis, and now allows for pH adjustments in the laboratory if the sample is returned within 14 days following sampling.

11. ASTM D 1688–12 (A–C), copper, AA direct aspiration, AA furnace; ASTM modified the method to allow the use of block digestion systems for trace metal analysis, and now allows for pH adjustments in the laboratory if the sample is returned within 14 days following sampling. ASTM also requires analysis of a continuing calibration blank and continuing calibration verification at a 10% frequency.

12. ASTM D 1691–12 (A, B), zinc, AA direct aspiration; ASTM modified the method to allow the use of block digestion systems for trace metal analysis, and now allows for pH adjustments in the laboratory if the sample is returned within 14 days following sampling.

13. ASTM D 1976–12, dissolved, total-recoverable, or total elements, inductively coupled plasma/atomic emission spectroscopy (ICP/AES); ASTM modified the method to allow block digestion systems for trace metal analysis.

14. ASTM D 3223–12, total mercury, cold vapor, manual; ASTM modified the method to allow the use of block digestion systems for trace metal analysis, and requires analysis of a continuing calibration blank and continuing calibration verification at a 10% frequency.

15. ASTM D 3373–12, vanadium, AA furnace; ASTM modified the method to allow the use of block digestion systems for trace metal analysis, and requires analysis of a continuing calibration blank and continuing calibration verification at a 10% frequency. ASTM now allows for pH adjustments in the laboratory if the sample is returned within 14 days following sampling.

16. ASTM D 3557–12 (A–D), cadmium, AA direct aspiration, AA furnace, Voltammetry; ASTM modified the method to allow the use of block digestion systems for trace metal analysis, and requires analysis of a continuing calibration blank and continuing calibration verification at a 10% frequency. ASTM now allows for pH adjustments in the laboratory if the sample is returned within 14 days following sampling.

17. ASTM D 3590–11 (A, B), total Kjeldahl nitrogen, manual digestion and distillation or gas diffusion; semi-automated block digester colorimetric (distillation not required); ASTM revised the preservation method to allow storing samples at 2–6 °C, instead of the previous 4 °C. The method includes OI Analytical Flow Injection Analysis (FIA) performance data using an alternative copper sulfate catalyst in place of mercury (note: ''OI Analytical'' is a company name, not an acronym).

18. ASTM D 4382–12, barium, AA furnace; ASTM modified the method to allow the use of block digestion systems for trace metal analysis, and requires analysis of a continuing calibration blank and continuing calibration verification at a 10% frequency.

19. ASTM D 4658–09, sulfide ion, ion selective electrode; no substantive changes.

20. ASTM D 5257–11, dissolved hexavalent chromium, ion chromatography; ASTM recommends buffering samples containing very high levels of anionic species to a pH of 9–9.5, then filtering the sample and storing it at <6 °C for a holding time of 28 days to prevent reduction of Cr(VI) to Cr(III). ASTM added an allowance for alternate holding times in Sections 1.3 and 9.2 if the user ''demonstrates that holding time does not affect sample integrity per US EPA 40 CFR 136 . . .''

21. ASTM D 5673–10, dissolved elements and total-recoverable elements, ICP/MS; no substantive changes.

22. ASTM D 5907–13, filterable matter (total dissolved solids) and nonfilterable matter (total suspended solids), gravimetric, 180° gravimetric, 103–105° post washing of residue; no substantive changes.

23. ASTM D 6508–10, inorganic anions (fluoride, bromide, chloride, nitrite, nitrate, orthophosphate, and sulfate), capillary ion electrophoresis with indirect UV detection; no substantive changes.

24. ASTM D 7284–13, total cyanide, manual distillation with $MgCl_2$ followed by flow injection, gas diffusion amperometry; ASTM modified the method to include the use of a collector tube of the micro distillation apparatus with 1.5 ml of 1.0 M NaOH, and included information regarding the use of this collector tube in the procedure. ASTM also added information regarding the precision and bias associated with this method based on an interlaboratory study.

25. ASTM D 7511–12, total cyanide, segmented flow injection, in-line ultraviolet digestion, followed by gas diffusion amperometry; no substantive changes.

The following changes would apply to Table IC at 40 CFR part 136:

1. ASTM D 7065–11, nonylphenol, bisphenol A, p-tert-octylphenol, nonylphenol monoethoxylate, nonylphenol diethoxylate, gas chromatography/mass spectrometry (GC/MS); no substantive changes.

E. Changes to 40 CFR 136.3 To Include New United States Geological Survey (USGS) Methods

1. EPA proposes to add the USGS Methods I–2547–11 and I–2548–11 titled ''Colorimetric Determination of Nitrate Plus Nitrite in Water by Enzymatic Reduction, Automated Discrete Analyzer Methods,'' to Table IB for the analytes nitrate, nitrite, and combined nitrate-nitrite. Method I–2548–11 is a low level (analytical range) version of Method I–2547–11. They are both included in the same method title. The method can be found in USGS Survey Techniques and Methods, Book 5, Chapter B8. The method is available for free from the USGS Web site. This method follows the same procedure as in ATP Case No. N07–0003—Nitrate Elimination Company Inc.'s (NECi) Method N07–0003, Revision 9.0, March 2014, ''Method for Nitrate Reductase Nitrate-Nitrogen Analysis,'' which EPA also proposes to approve. Additional details on the ATP study and multi-laboratory validation can be found in Section E.1 below.

F. Changes to 40 CFR 136.3 to Include ATPs

To promote method innovation, EPA maintains a program that allows method developers to apply for EPA review of an alternative method to an existing approved method and potentially for EPA approval of that ATP. This ATP program is described for CWA applications at 40 CFR 136.4 and 136.5. EPA proposes for nationwide use six alternate test procedures. Based on EPA's review, the performance of these ATPs is equally effective as other methods already approved for measurement. These proposed new methods include: NECi Method N07–0003, ''Method for Nitrate Reductase Nitrate-Nitrogen Analysis;'' Timberline Instruments, LLC Method Ammonia-001, ''Determination of Inorganic Ammonia by Continuous Flow Gas Diffusion and Conductivity Cell Analysis;'' IDEXX Laboratories, Inc. Colilert®-18, ''Coliform/*E. coli* Enzyme Substrate Test for fecal coliforms in Wastewater;'' NCASI Method TNTP–W10900, ''Total (Kjeldahl) Nitrogen and Total Phosphorus in Pulp and Paper Biologically Treated Effluent by Alkaline Persulfate Digestion;'' Hach Company Method 10242, ''Simplified Spectrophotometric Measurement of Total Kjeldahl Nitrogen in Water and Wastewater;'' and Hach Company Method 10206, ''Spectrophotometric Measurement of Nitrate in Water and Wastewater.'' Descriptions of these new methods included for approval are as follows:

1. The Nitrate Elimination Company Inc. (NECi) Method N07–0003, ''Nitrate Reductase Nitrate-Nitrogen Analysis,'' Revision 9.0, dated March 2014 (The Nitrate Elimination Company, Inc 2014a). The analysis measures nitrate, nitrite, and combined nitrate-nitrite. NECi Method N07–0003 is a ''green'' alternative to the other approved methods which use cadmium, a known carcinogen for the reduction of nitrate to nitrite prior to analyses. NECi Method N07–003 uses automated discreet analysis and spectrophotometry to determine concentrations of nitrate and nitrite, combined or separately in wastewater. The method involves the following steps:

- Enzymatic reduction of nitrate in a sample to nitrite using eukaryotic nitrate reductase;
- Diazotizing the nitrite originally in the sample plus the reduced nitrate with sulfanilamide followed by coupling with N-(1-napthyl)ethylenediamine dihydrochloride under acidic conditions to form a highly colored azo dye;
- Colorimetric determination in which the absorbance of color at 546 nm is directly proportional to the concentration of the nitrite plus the reduced nitrate in the sample;
- Measurement of nitrite separately, if needed, by analysis of the sample while eliminating the reduction step;
- Subtraction of the nitrite value from that of the combined nitrate-nitrite value to measure nitrate separately if needed.

NECi Method N07–0003 can be obtained from The Nitrate Elimination Company, 334 Hecla Street, Lake Linden, Michigan, 49945. Telephone: 906–370–1130.

2. Timberline Instruments, LLC Method Ammonia-001, ''Determination of Inorganic Ammonia by Continuous Flow Gas Diffusion and Conductivity Cell Analysis,'' dated June 24, 2011 (Timberline Instruments, LLC 2011a). Timberline Ammonia-001 is an automated method that uses a gas permeation cell and a conductivity detector to determine concentrations of ammonia in wastewater. The method involves the following steps:

- An aqueous sample is combined with sodium hydroxide to a pH above 11 producing ammonia in a non-ionized form in solution.
- This solution is conveyed to a membrane assembly and the gaseous ammonia in the aqueous sample migrates through the hydrophobic membrane into a borate buffer absorption solution, which is then transported to a conductivity cell.
- The measured changes in conductivity are used to quantitate ammonia in the sample using an external calibration.

Timberline Instruments, LLC Method Ammonia-001 can be obtained from Timberline Instruments, LLC, 1880 South Flatiron Court, Boulder, Colorado 80301. Telephone: 303–440–8779.

3. IDEXX Laboratories, Inc., Colilert®-18, ''Coliform/*E. coli* Enzyme Substrate Test for fecal coliforms in Wastewater'' (ATP Case No. N09–0004). The method is identical to the already approved *E. coli* Colilert®-18 method, with one exception. The current method was designed for total coliforms and *E. coli*, at an incubation temperature of 35 ± 0.5°C for these organisms. The addendum to the IDEXX Colilert®-18 method allows for incubation at 44.5 ± 0.2°C for fecal coliforms.

The Colilert®-18 Coliform/*E. coli* Enzyme Substrate Test can be obtained from IDEXX Laboratories Inc., One IDEXX Drive, Westbrook, ME 04092, Telephone: 1–800–321–0707.

4. National Council for Air and Stream Improvement, Inc. (NCASI) Method TNTP–W10900, ''Total (Kjeldahl) Nitrogen (TKN) and Total Phosphorus in Pulp and Paper Biologically Treated Effluent by Alkaline Persulfate Digestion,'' dated June 2011 (National Council for Air and Stream Improvement, Inc. 2011a). Unlike the other ATPs in the proposed rule, this method is for measurements in pulp, paper and paperboard mill biologically treated effluent only. NCASI Method TNTP–W10900 uses an alkaline persulfate digestion procedure to convert inorganic and organic nitrogen containing compounds to nitrate and inorganic and organic phosphorus containing compounds to orthophosphate which are then measured using a spectrophotometer to determine the concentration of total Kjeldahl nitrogen and total phosphorus in a sample.

The method involves the following steps:

- Oxidation of the inorganic and organic nitrogen containing compounds to nitrate and the inorganic and organic

forms of phosphorus to orthophosphate by heating acidified, unfiltered samples in the presence of persulfate (a strong oxidizer) at 120°C and 15 psi positive pressure for 30 minutes.

• Analysis of the digestate for measurement of nitrate and orthophosphate using the approved colorimetric procedures.

NCASI Method TNTP–W10900 can be obtained from The National Council for Air and Stream Improvement, Inc., Publications Coordinator, P.O. Box 13318, Research Triangle Park, NC 27709–3318, Telephone: 919–941–6400.

5. Hach Company Method 10242, ''Simplified Spectrophotometric Measurement of Total Kjeldahl Nitrogen in Water and Wastewater,'' Revision 1.1, dated January 10, 2013 (Hach Company 2013a). Hach Company Method 10242 is a simplified green chemistry alternative to the other approved methods for measuring TKN. The method uses less toxic reagents (*e.g.,* eliminating the use of mercuric sulfate). Hach Company Method 10242 uses a spectrophotometer to measure the concentration of total Kjeldahl nitrogen in a sample.

The method involves the following steps:

• Oxidation of the inorganic and organic nitrogen containing compounds to nitrate by digestion with peroxodisulfate;

• Reaction of nitrate with 2,6-dimethylphenol in a solution of sulfuric and phosphoric acid to form nitrodimethylphenol;

• Spectrophotometric measurement of the nitrodimethylphenol in which the absorbance of color at 345 nm is directly proportional to the concentration of total nitrogen in the sample;

• Measurement of oxidized forms of nitrogen (nitrite + nitrate) in the original sample in a second test vial;

• Subtraction of the concentration of the oxidized forms of nitrogen from the total nitrogen concentration resulting in the concentration of total Kjeldahl nitrogen in the sample.

Hach Company Method 10242 can be obtained from Hach Company, 5600 Lindbergh Drive, Loveland, CO 80539. Telephone: 970–669–3050.

6. Hach Company Method 10206, ''Spectrophotometric Measurement of Nitrate in Water and Wastewater,'' Revision 2.1, dated January 10, 2013 (Hach Company 2013b). Hach Company Method 1206 is a ''green'' alternative to the other approved methods which use cadmium, a known carcinogen for the reduction of nitrate to nitrite prior to analyses. Hach Company Method 10206 uses a spectrophotometer to measure the concentration of nitrate or combined nitrate-nitrite in a sample.

The method involves the following steps:

• Reaction of nitrate with 2,6-dimethylphenol in a solution of sulfuric and phosphoric acid to form nitrodimethylphenol;

• Spectrophotometric measurement of the nitrodimethylphenol in which the absorbance of color at 345 nm is directly proportional to the concentration of nitrate or, if the sample has been preserved with sulfuric acid, combined nitrate-nitrite in the sample.

Hach Company Method 10206 can be obtained from Hach Company, 5600 Lindbergh Drive, Loveland, CO 80539. Telephone: 970–669–3050.

G. Changes to 40 CFR part 136 to Align With 40 CFR part 122

The procedures approved in 40 CFR part 136 are often required as part of an application for a NPDES Permit NPDES, for reports required to be submitted under NPDES permits and/or for other requests for quantitative or qualitative effluent data under 40 CFR parts 122 and 125. EPA is clarifying the language in 40 CFR 136.1, 136.2, and 136.3 so that the term ''Director'' as used in 40 CFR part 136 parallels that in 40 CFR part 122. These sections use the terms ''Administrator'' and ''State having an authorized program'' and define these terms in 136.3. EPA proposes to revise these provisions to substitute the single term ''Director'' and define ''Director'' in section 40 CFR 136.3(d) by cross-reference to the definition of ''Director'' in the NPDES regulations at section 40 CFR 122.2.

EPA recently revised 40 CFR part 122 to include a definition of ''sufficiently sensitive.'' The term is used to describe what approved methods are adequate for NPDES permits. 40 CFR part 136.6(a)(2) uses the same term ''sufficiently sensitive'' in a different context to describe how sensitive a modified method should be compared to the original method. 40 CFR 136.6(a)(2) currently states that the modified method must be sufficiently sensitive and meet or exceed performance of the approved method(s) for the analyte(s) of interest, as documented by meeting the initial and ongoing quality control requirements in the method.

EPA proposes to delete the words ''be sufficiently sensitive and'' from 40 CFR 136.6(a)(2) to eliminate unnecessary confusion. It will not change the requirements of 40 CFR 136.6(a)(2). If a method modification meets or exceeds the performance of the approved method, this includes sensitivity.

H. Corrections to 40 CFR Part 136

These changes consist of typographical errors, updates that went unnoticed during the last update to 40 CFR part 136 to methods from VCSBs, and technology updates to toxicity methods.

1. EPA proposes to make a number of clarifications and corrections to its Whole Effluent Toxicity acute and chronic methods manuals (Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, EPA–821–R–02–012, October 2002; Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, EPA/821/R–02/013, October 2002; and Methods for Measuring the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, EPA/821/R–02/014, October 2002) listed in Table IA. Clarifications include testing all concentrations rather than only high and low concentrations, definition of terms (*e.g.,* the acronym YCT—yeast, cereal leaves, and trout chow, is not defined), consistency corrections among the three manuals, notation that Cusum figure axes should be log scale, pH and temperature measurements should be done at the beginning of the test (rather than only at the end of the test), etc. Corrections also include deletion of unavailable products, typographical errors, etc.

2. EPA proposes to change the Standard Method listed for *E. coli* most probable number (MPN) in Tables IA and IH. During a previous revision, Standard Methods added sampling as section 9221B.1. As a result, section 9221B.1 in previously approved versions has become section 9221B.2. EPA proposes to change SM 9221B.1 to 9221B.2 in Tables IA and IH for *E. coli* MPN. The related footnotes in Tables IA and IH (12, 14 and 11, 13, respectively) are accurate and EPA does not propose to change them.

3. EPA proposes to change Table IA for Enterococci. EPA proposes to reinstate a line for Enterococci that was erroneously deleted in the 2012 Methods Update Rule. The line ''MPN, multiple tube'' with Standard Method 9230B–2007 should be added.

4. EPA proposes to change one of the Table IB hardness entries that currently states ''Ca plus Mg as their carbonates, by inductively coupled plasma or AA direct aspiration. (See Parameters 13 and 33).'' EPA proposes to revise the entry to ''Ca plus Mg as their carbonates, by any approved method for Ca and Mg (See Parameters 13 and 33), provided

that the sum of the lowest point of quantitation for Ca and Mg is below the NPDES permit requirement for Hardness.'' The rationale behind this change is that if one calcium and magnesium method approved by EPA can be used to calculate hardness, then other approved EPA methods should also be permitted to do so.

5. EPA proposes to edit Table IB, footnote 24. EPA proposes to delete ''p 14'' from the footnote because the method is not on that page.

6. EPA proposes to delete Method 200.5, in Table IB from the cobalt, molybdenum and thallium entries. These analytes have not undergone formal testing by this method, and this method should not have been approved for these analytes.

7. EPA proposes to remove the reference to costs in 40 CFR 136.3 because costs are not included in the referenced documents.

8. EPA proposes to remove the first instance of ''are'' in 40 CFR 136.3(e) because it is an error.

I. Changes to Table II at 40 CFR 136.3(e) to Required Containers, Preservation Techniques, and Holding Times

EPA proposes revisions to Table II at 40 CFR 136.3(e) to amend some of the current requirements.

1. EPA proposes to add rows to Table II that specify holding times for total/fecal coliforms, and fecal streptococci in Table IH. Currently these bacterial tests are unspecified. EPA proposes the same holding time requirements as the other bacterial tests.

2. EPA proposes to change the sodium thiosulfate concentrations in Table II for bacterial tests from 0.0008% sodium thiosulfate to 0.008%. EPA proposed this change in its last update to 40 CFR part 136 (75 FR 58066–58067), but inadvertently omitted it in the publication of the final rule.

3. EPA proposes to re-insert language that was accidentally deleted from footnote 5 of Table II during the last update to 40 CFR part 136. Footnote 5 currently reads ''ASTM D7365–09a specifies treatment options for samples containing oxidants (*e.g.,* chlorine). Also, Section 9060A of Standard Methods for the Examination of Water and Wastewater (20th and 21st editions) addresses dechlorination procedures.'' EPA proposes to revise the footnote to read ''ASTM D7365–09a specifies treatment options for samples containing oxidants (*e.g.,* chlorine) for cyanide analysis. Also, Section 9060A of Standard Methods for the Examination of Water and Wastewater (20th and 21st editions) addresses dechlorination procedures for microbiological analyses.'' The footnote needs to specify that treatment options for samples containing oxidants is specifically for cyanide analysis, and that the dechlorination procedures are specifically for microbiological analyses.

4. EPA seeks comment on how to approve variances to sample preservation, containers or holding times listed in Table II for specific dischargers. Before the 2012 Final Method Update Rule (FR 77: 29758), the regulation required parties requesting a variance from Table II for specific dischargers to send the request to the appropriate EPA regional office for review, and then for the regional office to send the request to the National ATP Coordinator at EPA Headquarters for review and recommendation. Following receipt of such recommendation, the regional office could approve a variance. In the 2012 Final Method Update Rule, EPA changed the requirement so that either the Regional ATP Coordinator or the permitting authority could approve an exception to Table II for specific dischargers. The primary rationale for this change, as stated in the preamble of the 2010 Proposed Method Update Rule (FR 76: 77742) was: ''EPA is revising the text at 136.3(e) to allow a party to explain, without a cumbersome waiver process, to their permitting or other authority their basis for an alternative approach.'' Giving this authority to either the Regional ATP Coordinator or the permitting authority speeds up the approval process. Also, the permitting authority is more likely to know about special circumstances surrounding the local dischargers (*e.g.,* unusual discharge matrices, remote locations, etc.).

This change in the approval process resulted in the following potential complications and EPA is interested in public comment on them. First, it created a parallel authority to approve variances to Table II for specific dischargers. A discharger could make a request to both the Regional ATP Coordinator and the permitting authority, receive contradictory answers, and then choose the answer that the discharger prefers. Second, when there are different authorities approving a Table II variance for specific dischargers, there is potential for the data and documentation required by one authority to differ significantly from that required by the other authority.

EPA seeks comment on potential paths forward that would eliminate these concerns, while streamlining the process so that approval can be granted within the EPA region or by the state permitting authority. One possibility is for the permitting authority and the Regional ATP Coordinator to approve Table II variances for specific dischargers collaboratively. The permitting authority could provide the initial review and approval, and then approved requests could be sent to the Regional ATP Coordinator for final review and approval. Both organizations would need to agree for specific dischargers to be allowed Table II variances. Another option is to give the Regional ATP Coordinator exclusive rights to approve Table II variances for specific dischargers. Another option is to give the permitting authority exclusive rights to approve Table II variances. Other options are also possible, such as leaving 40 CFR 136.3(e) unchanged.

EPA also seeks comment on what data should be submitted to support a request for a Table II variance for a specific discharger. 40 CFR 136.3(e) requires that data be included with any request to modify Table II requirements for a specific discharger. The data would need to prove that the variance does not compromise the analytical results.

J. Clarifications/Corrections to ATP Procedures in 40 CFR 136.4, 136.5 and Allowed Modifications in 136.6

40 CFR 136.4 and 136.5 describe EPA procedures for obtaining approval to use an alternate test procedures either on a national basis, or for limited use by dischargers or facilities specified in the approval. In the 2012 Method Update Rule, EPA made several clarifying changes to the language of these sections. At the same time, however, in many places in 40 CFR 136.4 and 136.5 where the phrase ''Regional Alternate Test Procedures Coordinator'' or ''Regional ATP Coordinator'' appears, EPA inadvertently also inserted the phrase ''or permitting authority'' following the phrase. This error resulted from the use of the ''search and replace'' function on the computer. The effect of the change was to inadvertently authorize *State* permitting authorities to approve ATPs for limited use within the State. EPA never intended this result as is demonstrated by two facts. First, in its proposal for the 2012 Update, EPA did not propose to authorize State NPDES permitting authorities to approve limited use ATPs. Second, the rule states that the approval may be restricted to specific dischargers or facilities, or to all dischargers or facilities ''specified in the approval *for the Region.''* (emphasis added). This language evidences EPA's intent that the Region—not the state—would be

authorized to issue any such limited use ATP approval. Finally, as further evidence of EPA's intent, in several places, the text of the rule makes more sense if read to authorize only the Regional ATP Coordinator, and not the State permitting authority, to approve limited use ATPs. For example, 40 CFR 136.5(d)(1) provides that after a review of the application by the Alternate Test Procedure Regional ATP Coordinator or permitting authority, the Regional ATP Coordinator or permitting authority notifies the applicant and the appropriate State agency of approval or rejection of the use of the alternate test procedure.

As currently written, if the State is acting on a request for approval, the regulation would require the State to inform itself of its own action in approving or rejecting the ATP, a somewhat superfluous requirement.

Consequently, EPA proposes to delete all instances of ''or permitting authority'' from 40 CFR 136.4 and 136.5 to correct this error and revise the rule text to its original intent. Based on this revision, EPA and EPA alone would have the authority to approve limited use ATPs.

EPA also proposes changes to 40 CFR 136.4 and 136.5 to clarify the process for nationwide approval and the Regional ATP Coordinator's role in limited use ATP approvals. These changes do not significantly change the process, the intent is to make wording simpler and clearer.

Finally, EPA proposes to add language to 40 CFR 136.6(b)(1) to clarify that if a method user is uncertain whether or not a modification is allowed under 40 CFR 136.6, the user should contact either its Director or EPA Regional ATP Coordinator.

K. Changes to Appendix B to 40 CFR part 136—Definition and Procedure for the Determination of the MDL

EPA proposes revisions to the procedure for determination of the MDL primarily to address laboratory blank contamination and to better account for intra-laboratory variability. EPA's consideration of revisions to the MDL procedure for this rulemaking is specific to these revisions, and other changes to the procedure are outside the scope of this action. The proposed changes originated from The National Environmental Laboratory Accreditation Conference Institute and also reflect review by EPA, states, and commercial laboratories. The proposed revisions address the following issues and would add new requirements.

Background contamination: laboratories would be required to evaluate the MDL to account for background levels of contamination. As laboratory methods become more and more sensitive, background levels of contamination are more likely to contribute to the result. This modification would reduce false positive detects.

MDLs that represent multiple instruments: if a laboratory uses MDL values that represent multiple instruments, then the laboratory would be required to calculate the MDL using spiked samples and blank samples from all of these instruments. Currently, laboratories can run all of their MDL samples on the most sensitive instrument, and then use that MDL for other instruments. This modification will make the MDL more representative of the laboratory's actual capability.

Ongoing MDL quarterly verification: laboratories would be required to check their MDL values once a quarter. Currently, laboratories can run MDL samples once a year under the most ideal circumstances (*e.g.,* immediately after the instrument has been serviced or after an annual maintenance routine). Quarterly evaluation will determine if the detection limit has significantly drifted during the year. Laboratories would be exempt from running these samples for a method during quarters when no samples are run using that method.

EPA requests comment on whether it should adopt these proposed changes, in part, or in whole.

V. Statutory and Executive Order Reviews

A. Executive Order 12866: Regulatory Planning and Review and Review and Executive Order 13563: Improving Regulation and Regulatory Review

This rule is not a significant regulatory action and was therefore not submitted to the Office of Management and Budget for review.

B. Paperwork Reduction Act

This action does not impose an information collection burden under the PRA. This rule does not impose any information collection, reporting, or recordkeeping requirements. This proposal would merely add or revise CWA test procedures.

C. Regulatory Flexibility Act

I certify that this action would not have a significant economic impact on a substantial number of small entities under the RFA. This action will not impose any requirements on small entities. This action would approve new and revised versions of CWA testing procedures. Generally, these changes would have a positive impact on small entities by increasing method flexibility, thereby allowing entities to reduce costs by choosing more cost-effective methods. In general, EPA expects the proposed revisions would lead to few, if any, increased costs. As explained previously, most of the proposed changes clarify procedures for EPA approval of ATPs, clarify or improve the instructions in the method, update the technology used in the method, improve the QC instructions, make editorial corrections, or reflect the most recent approval year of an already approved method. In some cases, the proposal would add alternatives to currently approved methods for a particular analyte (*e.g.* Method N07–0003 for Nitrate Reductase Nitrate-Nitrogen Analysis). Because these methods would be alternatives rather than requirements, there are no direct costs associated with their proposal. EPA proposes methods that would be incorporated by reference. If a permittee elected to use these methods, they could incur a small cost associated with obtaining these methods. See Section IV.B. Finally, the proposed changes to the MDL procedure would lead to limited increased costs. In the vast majority of cases, laboratories already collect samples that could be used in the revised procedure and/or would simply adjust the time period of collection. The total number of MDL samples run annually would only increase to any appreciable extent for laboratories that own many instruments. EPA has not estimated costs for these cases, because such costs, if incurred, would be negligible in comparison to overall laboratory expenditures.

D. Unfunded Mandates Reform Act

This action does not contain any unfunded mandate as described in UMRA, 2 U.S.C. 1531–1538, and does not significantly or uniquely affect small governments. The action imposes no enforceable duty on any state, local or tribal governments or the private sector.

E. Executive Order 13132: Federalism

This proposed rule does not have federalism implications. It will not have substantial direct effects on the states, on the relationship between the national government and the states, or on the distribution of power and responsibilities among the various levels of government.

F. Executive Order 13175: Consultation and Coordination with Indian Tribal Governments

This proposed rule does not have tribal implications as specified in Executive Order 13175. This rule would merely approve new and revised versions of test procedures. EPA does not expect the proposal would lead to any costs to any tribal governments, and if incurred, projects they would be minimal. Thus, Executive Order 13175 does not apply to this action.

G. Executive Order 13045: Protection of Children from Environmental Health Risks and Safety Risks

EPA interprets EO 13045 as applying only to those regulatory actions that concern environmental health or safety risks that the EPA has reason to believe may disproportionately affect children, per the definition of ''covered regulatory action'' in section 2–202 of the Executive Order. This action is not subject to Executive Order 13045 because it does not concern an environmental health risk or safety risk.

H. Executive Order 13211: Actions that Significantly Affect Energy Supply, Distribution, or Use

This action is not subject to Executive Order 13211 because it is not a significant regulatory action under Executive Order 12866.

I. National Technology Transfer and Advancement Act of 1995

This action involved technical standards. The EPA proposes to approve the use of technical standards developed and recommended by the Standard Methods Committee and ASTM International for use in compliance monitoring where EPA determined that those standards meet the needs of CWA programs. As explained in Section IV.C, EPA does not propose to add one SM method because it did not receive data to demonstrate that the method had undergone full inter-laboratory validation. EPA proposes all other methods recommended by VCSBs in advance of the proposed rule.

J. Executive Order 12898: Federal Actions To Address Environmental Justice in Minority Populations and Low-Income Populations

The EPA believes the human health or environmental risk addressed by this action will not have potential disproportionately high and adverse human health or environmental effects on minority, low-income or indigenous populations.

List of Subjects in 40 CFR Part 136

Environmental protection, Incorporation by reference, Reporting and recordkeeping requirements, Test procedures, Water pollution control.

Dated: February 5, 2015.

Gina McCarthy,

Administrator.

For the reasons set out in the preamble, title 40, chapter I of the Code of Federal Regulations is proposed to be amended as follows:

PART 136—GUIDELINES ESTABLISHING TEST PROCEDURES FOR THE ANALYSIS OF POLLUTANTS

■ 1. The authority citation for part 136 continues to read as follows:

Authority: Secs. 301, 304(h), 307 and 501(a), Pub. L. 95–217, 91 Stat. 1566, *et seq.*

(33 U.S.C. 1251, *et seq.*) (the Federal Water Pollution Control Act Amendments of 1972 as amended by the Clean Water Act of 1977).

■ 2. Section 136.1 is amended by revising paragraph (a) to read as follows:

§ 136.1 Applicability.

(a) The procedures prescribed herein shall, except as noted in §§ 136.4, 136.5, and 136.6, be used to perform the measurements indicated whenever the waste constituent specified is required to be measured for:

(1) An application submitted to the Director and/or reports required to be submitted under NPDES permits or other requests for quantitative or qualitative effluent data under parts 122 to 125 of this chapter; and

(2) Reports required to be submitted by dischargers under the NPDES established by parts 124 and 125 of this chapter; and

(3) Certifications issued by States pursuant to section 401 of the Clean Water Act (CWA), as amended.

* * * * *

■ 3. Section 136.2 is amended by revising paragraph (d) to read as follows:

§ 136.2 Definitions.

* * * * *

(d) *Director* means the director as defined in 40 CFR 122.2.

* * * * *

■ 4. In § 136.3:

■ a. Revise paragraph (a) introductory text and tables IA, IB, IC, ID, IF, IG, and IH.

■ b. Revise paragraphs (b) introductory text, (b)(8)(iv), (b)(8)(v), (b)(8)(xiii), (b)(8)(xv), (b)(10)(viii), (b)(10)(x) through (lviii), (b)(10)(lxi) through (lxiii), (b)(10)(lxviii), (b)(15)(v), (b)(15)(viii) through (x), (b)(15)(xii), (b)(15)(xiii), (b)(15)(xv) through (xvii), (b)(15)(xxii) through (xxiv), (b)(15)(xxx), (b)(15)(xxxv), (b)(15)(xxxvii), (b)(15)(xxxix), (b)(15)(xlii), (b)(15)(l), (b)(15)(lii), (b)(15)(lv), (b)(15)(lviii), (b)(15)(lxi), (b)(15)(lxvi), and (b)(15)(lxviii).

■ c. Redesignate paragraphs (b)(19)(vii) and (viii) as paragraphs (b)(19)(ix) and (x), respectively.

■ d. Add paragraphs (b)(19)(vii) and (viii).

■ e. Revise paragraphs (b)(20)(i) through (iv).

■ f. Remove paragraph (b)(20)(v).

■ g. Revise paragraph (b)(25).

■ h. Redesignate paragraphs (b)(33) and (34) as paragraphs (b)(35) and (36), respectively, and redesignate paragraphs (b)(26) through (32) as paragraphs (b)(27) through (33), respectively.

■ i. Add paragraph (b)(26).

■ j. Add paragraph (b)(34).

■ k. Revise newly redesignated paragraph (b)(35).

■ l. Revise paragraph (c) and the table in paragraph (e).

The revisions and additions read as follows:

§ 136.3 Identification of test procedures.

(a) Parameters or pollutants, for which methods are approved, are listed together with test procedure descriptions and references in Tables IA, IB, IC, ID, IE, IF, IG, and IH of this section. The methods listed in Tables IA, IB, IC, ID, IE, IF, IG, and IH are incorporated by reference, see paragraph (b) of this section, with the exception of EPA Methods 200.7, 601–613, 624.1, 625.1, 1613, 1624, and 1625. The full texts of Methods 601–613, 624.1, 625.1, 1613, 1624, and 1625 are printed in appendix A of this part, and the full text of Method 200.7 is printed in appendix C of this part. The full text for determining the method detection limit when using the test procedures is given in appendix B of this part. In the event of a conflict between the reporting requirements of 40 CFR parts 122 and 125 and any reporting requirements associated with the methods listed in these tables, the provisions of 40 CFR parts 122 and 125 are controlling and will determine a permittee's reporting requirements. The full text of the referenced test procedures are incorporated by reference into Tables IA, IB, IC, ID, IE, IF, IG, and IH. The date after the method number indicates the latest editorial change of the method. The discharge parameter values for which reports are required must be determined by one of the standard analytical test procedures incorporated by reference and described in Tables IA,

IB, IC, ID, IE, IF, IG, and IH or by any alternate test procedure which has been approved by the Administrator under the provisions of paragraph (d) of this section and §§ 136.4 and 136.5. Under certain circumstances paragraph (c) of this section, § 136.5(a) through (d) or 40 CFR 401.13, other additional or alternate test procedures may be used.

TABLE IA—LIST OF APPROVED BIOLOGICAL METHODS FOR WASTEWATER AND SEWAGE SLUDGE

Parameter and units	Method [1]	EPA	Standard methods	AOAC, ASTM, USGS	Other
Bacteria:					
1. Coliform (fecal), number per 100 mL or number per gram dry weight.	Most Probable Number (MPN), 5 tube, 3 dilution, or.	p. 132 [3] 1680 [11 15] 1681 [11 20]	9221 C E–2006		
	Multiple tube/multiple well, or.	.....		.....	Colilert-18® [13 18 29]
	Membrane filter (MF) [2], single step.	p. 124 [3]	9222 D–2006 [30]	B–0050–85 [4].	
2. Coliform (fecal) in presence of chlorine, number per 100 mL.	MPN, 5 tube, 3 dilution, or	p. 132 [3]	9221 C E–2006		
	MF [2], single step [5]	p. 124 [3]	9222 D–2006 [30]		
3. Coliform (total), number per 100 mL.	MPN, 5 tube, 3 dilution, or	p. 114 [3]	9221 B–2006		
	MF [2], single step or two step.	p. 108 [3]	9222 B–2006	B–0025–85 [4].	
4. Coliform (total), in presence of chlorine, number per 100 mL.	MPN, 5 tube, 3 dilution, or	p. 114 [3]	9221 B–2006		
	MF [2] with enrichment [5]	p. 111 [3]	9222 B – 2006		
5. *E. coli,* number per 100 mL [21]	MPN [6 8 16] multiple tube, or	.....	9221B.2–2006/ 9221F–2006 [12 14]		
	multiple tube/multiple well, or.	.....	9223 B–2004 [13]	991.15 [10] ..	Colilert® [13 18] Colilert-18® [13 17 18]
	MF [2 6 7 8] single step	1603 [22]		.....	mColiBlue-24® [19]
6. Fecal streptococci, number per 100 mL.	MPN, 5 tube, 3 dilution, or	p. 139 [3]	9230 B–2007		
	MF [2], or	p. 136 [3]	9230 C–2007	B–0055–85 [4].	
	Plate count	p. 143 [3].			
7. Enterococci, number per 100 mL [21].	MPN, 5 tube, 3 dilution, or	p. 139 [3]	9230 B–2007		
	MPN [6 8], multiple tube/multiple well, or.	.....	9230 D–2007	D6503–99 [9].	Enterolert® [13 24]
	MF [2 6 7 8] single step or	1600 [25]	9230 C–2007		
	Plate count	p. 143 [3].			
8. *Salmonella*, number per gram dry weight [11].	MPN multiple tube	1682 [23].			
Aquatic Toxicity:					
9. Toxicity, acute, fresh water organisms, LC_{50}, percent effluent.	*Ceriodaphnia dubia* acute	2002.0 [26].			
	Daphnia puplex and *Daphnia magna* acute.	2021.0 [26].			
	Fathead Minnow, *Pimephales promelas,* and Bannerfin shiner, *Cyprinella leedsi,* acute.	2000.0 [26].			
	Rainbow Trout, *Oncorhynchus mykiss,* and brook trout, *Salvelinus fontinalis,* acute.	2019.0 [26].			
10. Toxicity, acute, estuarine and marine organisms of the Atlantic Ocean and Gulf of Mexico, LC_{50}, percent effluent.	Mysid, *Mysidopsis bahia,* acute.	2007.0 [26].			
	Sheepshead Minnow, *Cyprinodon variegatus,* acute.	2004.0 [26].			

TABLE IA—LIST OF APPROVED BIOLOGICAL METHODS FOR WASTEWATER AND SEWAGE SLUDGE—Continued

Parameter and units	Method [1]	EPA	Standard methods	AOAC, ASTM, USGS	Other
	Silverside, *Menidia beryllina, Menidia menidia,* and *Menidia peninsulae,* acute.	2006.0 [26].			
11. Toxicity, chronic, fresh water organisms, NOEC or IC_{25}, percent effluent.	Fathead minnow, *Pimephales promelas,* larval survival and growth.	1000.0 [27].			
	Fathead minnow, *Pimephales promelas,* embryo-larval survival and teratogenicity.	1001.0 [27].			
	Daphnia, *Ceriodaphnia dubia,* survival and reproduction.	1002.0 [27].			
	Green alga, *Selenastrum capricornutum,* growth.	1003.0 [27].			
12. Toxicity, chronic, estuarine and marine organisms of the Atlantic Ocean and Gulf of Mexico, NOEC or IC_{25}, percent effluent.	Sheepshead minnow, *Cyprinodon variegatus,* larval survival and growth.	1004.0 [28].			
	Sheepshead minnow, *Cyprinodon variegatus,* embryo-larval survival and teratogenicity.	1005.0 [28].			
	Inland silverside, *Menidia beryllina,* larval survival and growth.	1006.0 [28].			
	Mysid, *Mysidopsis bahia,* survival, growth, and fecundity.	1007.0 [28].			
	Sea urchin, *Arbacia punctulata,* fertilization.	1008.0 [28].			

Table IA notes:

[1] The method must be specified when results are reported.

[2] A 0.45-μm membrane filter (MF) or other pore size certified by the manufacturer to fully retain organisms to be cultivated and to be free of extractables which could interfere with their growth.

[3] Microbiological Methods for Monitoring the Environment, Water, and Wastes, EPA/600/8–78/017. 1978. US EPA.

[4] U.S. Geological Survey Techniques of Water-Resource Investigations, Book 5, Laboratory Analysis, Chapter A4, Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples. 1989. USGS.

[5] Because the MF technique usually yields low and variable recovery from chlorinated wastewaters, the Most Probable Number method will be required to resolve any controversies.

[6] Tests must be conducted to provide organism enumeration (density). Select the appropriate configuration of tubes/filtrations and dilutions/volumes to account for the quality, character, consistency, and anticipated organism density of the water sample.

[7] When the MF method has been used previously to test waters with high turbidity, large numbers of noncoliform bacteria, or samples that may contain organisms stressed by chlorine, a parallel test should be conducted with a multiple-tube technique to demonstrate applicability and comparability of results.

[8] To assess the comparability of results obtained with individual methods, it is suggested that side-by-side tests be conducted across seasons of the year with the water samples routinely tested in accordance with the most current Standard Methods for the Examination of Water and Wastewater or EPA alternate test procedure (ATP) guidelines.

[9] Annual Book of ASTM Standards-Water and Environmental Technology, Section 11.02. 2000, 1999, 1996. ASTM International.

[10] Official Methods of Analysis of AOAC International. 16th Edition, 4th Revision, 1998. AOAC International.

[11] Recommended for enumeration of target organism in sewage sludge.

[12] The multiple-tube fermentation test is used in 9221B.2–2006. Lactose broth may be used in lieu of lauryl tryptose broth (LTB), if at least 25 parallel tests are conducted between this broth and LTB using the water samples normally tested, and this comparison demonstrates that the false-positive rate and false-negative rate for total coliform using lactose broth is less than 10 percent. No requirement exists to run the completed phase on 10 percent of all total coliform-positive tubes on a seasonal basis.

[13] These tests are collectively known as defined enzyme substrate tests, where, for example, a substrate is used to detect the enzyme β-glucuronidase produced by *E. coli.*

[14] After prior enrichment in a presumptive medium for total coliform using 9221B.2–2006, all presumptive tubes or bottles showing any amount of gas, growth or acidity within 48 h ± 3 h of incubation shall be submitted to 9221F–2006. Commercially available EC–MUG media or EC media supplemented in the laboratory with 50 μg/mL of MUG may be used.

[15] Method 1680: Fecal Coliforms in Sewage Sludge (Biosolids) by Multiple-Tube Fermentation Using Lauryl-Tryptose Broth (LTB) and EC Medium, EPA–821–R–14–009. September 2014. U.S. EPA.

[16] Samples shall be enumerated by the multiple-tube or multiple-well procedure. Using multiple-tube procedures, employ an appropriate tube and dilution configuration of the sample as needed and report the Most Probable Number (MPN). Samples tested with Colilert® may be enumerated with the multiple-well procedures, Quanti-Tray® and the MPN calculated from the table provided by the manufacturer.

[17] Colilert-18® is an optimized formulation of the Colilert® for the determination of total coliforms and *E. coli* that provides results within 18 h of incubation at 35°C rather than the 24 h required for the Colilert® test and is recommended for marine water samples.

[18] Descriptions of the Colilert®, Colilert-18®, and Quanti-Tray® may be obtained from IDEXX Laboratories, Inc.

[19] A description of the mColiBlue24® test, is available from Hach Company.

[20] Method 1681: Fecal Coliforms in Sewage Sludge (Biosolids) by Multiple-Tube Fermentation using A–1 Medium, EPA–821–R–06–013. July 2006. U.S. EPA.

[21] Recommended for enumeration of target organism in wastewater effluent.

[22] Method 1603: *Escherichia coli* (*E. coli*) in Water by Membrane Filtration Using Modified membrane-Thermotolerant *Escherichia coli* Agar (modified mTEC), EPA–821–R–14–010. September 2014. U.S. EPA.
[23] Method 1682: *Salmonella* in Sewage Sludge (Biosolids) by Modified Semisolid Rappaport-Vassiliadis (MSRV) Medium, EPA–821–R–14–012. July 2014. U.S. EPA.
[24] A description of the Enterolert® test may be obtained from IDEXX Laboratories Inc.
[25] Method 1600: Enterococci in Water by Membrane Filtration Using membrane-Enterococcus Indoxyl-β-D-Glucoside Agar (mEI), EPA–821–R–14–011. September 2014. U.S. EPA.
[26] Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, EPA–821–R–02–012. Fifth Edition, October 2002. U.S. EPA.
[27] Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, EPA–821–R–02–013. Fourth Edition, October 2002. U.S. EPA.
[28] Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, EPA–821–R–02–014. Third Edition, October 2002. U.S. EPA.
[29] Colilert-18® is an optimized formulation of the Colilert® for the determination of total coliforms and *E. coli* that has been adapted to detect fecal coliforms. To use Colilert-18® to assay for fecal coliforms, the incubation temperature is 44.5 + 0.2°C. This test is recommended for wastewater samples.
[30] The verification frequency is at least five typical and five atypical colonies per sampling site on the day of sample collection and analysis.

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
1. Acidity, as $CaCO_3$, mg/L.	Electrometric endpoint or phenolphthalein endpoint.	.....	2310 B–2011	D1067–11	I–1020–85. [2]
2. Alkalinity, as $CaCO_3$, mg/L.	Electrometric or Colorimetric titration to pH 4.5, Manual.	.....	2320 B–1997	D1067–11	973.43 [3], I–1030–85. [2]
	Automatic	310.2 (Rev. 1974) [1].	.....	.....	I–2030–85. [2]
3. Aluminum—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration [36].	.....	3111 D–2011 or 3111 E–2011.	.....	I–3051–85. [2]
	AA furnace	.....	3113 B–2010.		
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14[3], I–4471–97. [50]
	Direct Current Plasma (DCP) [36].	.....	.....	D4190–08	See footnote. [34]
	Colorimetric (Eriochrome cyanine R).	.....	3500–Al B–2011.		
4. Ammonia (as N), mg/L	Manual distillation [6] or gas diffusion (pH > 11), followed by any of the following:	350.1, Rev. 2.0 (1993).	4500–NH_3 B–2011	.....	973.49. [3]
	Nesslerization	.....	.....	D1426–08 (A) ..	973.49 [3], I–3520–85. [2]
	Titration	.....	4500–NH_3 C–2011.		
	Electrode	.....	4500–NH_3 D–2011 or E–2011.	D1426–08 (B).	
	Manual phenate, salicylate, or other substituted phenols in Berthelot reaction based methods.	.....	4500–NH_3 F–2011	.....	See footnote. [60]
	Automated phenate, salicylate, or other substituted phenols in Berthelot reaction based methods.	350.1 [30], Rev. 2.0 (1993).	4500–NH_3 G–2011 ..... 4500–NH_3 H–2011	.....	I–4523–85. [2]
	Automated electrode	.....	.....	.....	See footnote. [7]
	Ion Chromatography	.....	.....	D6919–09.	
	Automated gas diffusion, followed by conductivity cell analysis.	.....	.....	.....	Timberline Ammonia–001 [74]
5. Antimony—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration [36].	.....	3111 B–2011.		
	AA furnace	.....	3113 B–2010.		
	STGFAA	200.9, Rev. 2.2 (1994).			

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4471–97. [50]
6. Arsenic-Total, [4] mg/L	Digestion [4], followed by any of the following:	206.5 (Issued 1978) [1].			
	AA gaseous hydride		3114 B–2011 or 3114 C–2011	D2972–08 (B)	I–3062–85. [2]
	AA furnace		3113 B–2010	D2972–08 (C)	I–4063–98. [49]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12.	
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4020–05. [70]
	Colorimetric (SDDC).		3500–As B–2011	D2972–08 (A)	I–3060–85. [2]
7. Barium-Total, [4] mg/L	Digestion[4], followed by any of the following:				
	AA direct aspiration [36].		3111 D–2011		I–3084–85. [2]
	AA furnace		3113 B–2010	D4382–12.	
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011		I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14[3], I–4471–97. [50]
	DCP [36]				See footnote. [34]
8. Beryllium—Total, [4] mg/L	Digestion [4], followed by any of the following:				
	AA direct aspiration		3111 D–2011 or 3111 E–2011.	D3645–08 (A)	I–3095–85. [2]
	AA furnace		3113 B–2010	D3645–08 (B).	
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4471–97. [50]
	DCP			D4190–08	See footnote. [34]
	Colorimetric (aluminon).		See footnote. [61]		
9. Biochemical oxygen demand (BOD5), mg/L.	Dissolved Oxygen Depletion.		5210 B–2011		973.44 [3], p. 17 [9], I–1578–78 [8], See footnote. [10, 63]
10. Boron—Total, [37] mg/L	Colorimetric (curcumin)		4500–B B–2011		I–3112–85. [2]
	ICP/AES	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4471–97. [50]
	DCP			D4190–08	See footnote. [34]
11. Bromide, mg/L	Electrode			D1246–10	I–1125–85. [2]
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2011, C–2011, D–2011.	D4327–03	993.30. [3]
	CIE/UV		4140 B–2011	D6508–10, D6508, Rev. 2 [54].	
12. Cadmium—Total, [4] mg/L.	Digestion [4], followed by any of the following:				

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	AA direct aspiration [36].	.....	3111 B–2011 ..... or 3111 C–2011	D3557–12 (A or B).	974.27 [3], p. 37 [9], I–3135–85 [2] or I–3136–85. [2]
	AA furnace	.....	3113 B–2010	D3557–12 (D) ..	I–4138–89. [51]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–1472–85 [2] or I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4471–97. [50]
	DCP [36]	.....	.....	D4190–08	See footnote. [34]
	Voltametry [11]	.....	.....	D3557–12 (C).	
	Colorimetric (Dithizone).	.....	3500–Cd–D–1990.		
13. Calcium—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration	.....	3111 B–2011	D511–09(B)	I–3152–85. [2]
	ICP/AES	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	.....	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14. [3]
	DCP	.....	.....	.....	See footnote. [34]
	Titrimetric (EDTA) ..	.....	3500–Ca B–2011	D511–09 (A).	
	Ion Chromatography.	.....	.....	D6919–09.	
14. Carbonaceous biochemical oxygen demand ($CBOD_5$), mg/L [12].	Dissolved Oxygen Depletion with nitrification inhibitor.	.....	5210 B–2011	.....	See footnote. [35, 63]
15. Chemical oxygen demand (COD), mg/L.	Titrimetric	410.3 (Rev. 1978) [1].	5220 B–2011 ..... or C–2011	D1252–06 (A) ..	973.46 [3], p. 17 [9], I–3560–85. [2]
	Spectrophotometric, manual or automatic.	410.4, Rev. 2.0 (1993).	5220 D–2011	D1252–06 (B) ..	See footnotes. [13, 14], I–3561–85. [2]
16. Chloride, mg/L	Titrimetric: (silver nitrate)	.....	4500–Cl^- B–2011	D512–04 (B)	I–1183–85. [2]
	(Mercuric nitrate)	.....	4500–Cl^- C–2011	D512–04 (A)	973.51 [3], I–1184–85. [2]
	Colorimetric: manual.	.....	.....	.....	I–1187–85. [2]
	Automated (ferricyanide).	.....	4500–Cl^- E–2011	.....	I–2187–85. [2]
	Potentiometric Titration.	.....	4500–Cl^- D–2011.		
	Ion Selective Electrode.	.....	.....	D512–04 (C).	
	Ion Chromatography.	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2011 or 4110 C–2011.	D4327–03	993.30 [3], I–2057–90. [51]
	CIE/UV	.....	4140 B–2011	D6508–10, D6508, Rev. 2 [54].	
17. Chlorine—Total residual, mg/L.	Amperometric direct	.....	4500–Cl D–2011	D1253–08.	
	Amperometric direct (low level).	.....	4500–Cl E–2011.		
	Iodometric direct	.....	4500–Cl B–2011.		
	Back titration ether end-point [15].	.....	4500–Cl C–2011.		
	DPD–FAS	.....	4500–Cl F–2011.		
	Spectrophotometric, DPD.	.....	4500–Cl G–2011.		
	Electrode	.....	.....	.....	See footnote. [16]
17A. Chlorine-Free Available, mg/L.	Amperometric direct	.....	4500–Cl D–2011	D1253–08.	
	Amperometric direct (low level).	.....	4500–Cl E–2011.		
	DPD–FAS	.....	4500–Cl F–2011.		
	Spectrophotometric, DPD.	.....	4500–Cl G–2011.		

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
18. Chromium VI dissolved, mg/L.	0.45-micron filtration followed by any of the following:				
	AA chelation-extraction.	.....	3111 C–2011	.....	I–1232–85. [2]
	Ion Chromatography.	218.6, Rev. 3.3 (1994).	3500–Cr C–2011	D5257–11	993.23.
	Colorimetric (diphenyl-carbazide).	.....	3500–Cr B–2011	D1687–12 (A) ..	I–1230–85. [2]
19. Chromium—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration [36].	.....	3111 B–2011	D1687–12 (B) ..	974.27 [3], I–3236–85. [2]
	AA chelation-extraction.	.....	3111 C–2011.		
	AA furnace	.....	3113 B–2010	D1687–12 (C) ..	I–3233–93. [46]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68], 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4020–05. [70]
	DCP [36]	.....	.....	D4190–08	See footnote. [34]
	Colorimetric (diphenyl-carbazide).	.....	3500–Cr B–2011.		
20. Cobalt—Total, [4] mg/L	Digestion [4], followed by any of the following:				
	AA direct aspiration	.....	3111 B–2011 or 3111 C–2011.	D3558–08 (A or B).	p. 37 [9], I–3239–85. [2]
	AA furnace	.....	3113 B–2010	D3558–08 (C) ..	I–4243–89. [51]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4020–05. [70]
	DCP	.....	.....	D4190–08	See footnote. [34]
21. Color, platinum cobalt units or dominant wavelength, hue, luminance purity.	Colorimetric (ADMI)	.....	2120 F–2011	.....	See footnote. [18]
	(Platinum cobalt) Spectrophotometric.	.....	2120 B–2011	.....	I–1250–85. [2]
22. Copper—Total, [4] mg/L	Digestion [4], followed by any of the following:				
	AA direct aspiration [36].	.....	3111 B–2011 or 3111 C–2011	D1688–12 (A or B).	974.27 [3], p. 37 [9], I–3270–85 [2] or I–3271–85. [2]
	AA furnace	.....	3113 B–2010	D1688–12 (C) ..	I–4274–89. [51]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4020–05. [70]
	DCP [36]	.....	.....	D4190–08	See footnote. [34]
	Colorimetric (Neocuproine).	.....	3500–Cu B–2011.		
	Colorimetric (Bathocuproine).	.....	3500–Cu C–2011	.....	See footnote. [19]
23. Cyanide—Total, mg/L	Automated UV digestion/distillation and Colorimetry.	.....	.....	.....	Kelada–01. [55]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	Segmented Flow Injection, In-Line Ultraviolet Digestion, followed by gas diffusion amperometry.	.....	.....	D7511–12.	
	Manual distillation with $MgCl_2$, followed by any of the following:	335.4, Rev. 1.0 (1993) [57].	4500–CN − B–2011 and C–2011.	D2036–09(A), D7284–13.	10–204–00–1–X. [56]
	Flow Injection, gas diffusion amperometry.	.....	.....	D2036–09(A) D7284–13.	
	Titrimetric	.....	4500–CN − D–2011	D2036–09(A)	p. 22. [9]
	Spectrophotometric, manual.	.....	4500–CN − E–2011	D2036–09(A)	I–3300–85. [2]
	Semi-Automated [20]	335.4, Rev. 1.0 (1993) [57].	.....	.....	10–204–00–1–X [56], I–4302–85. [2]
	Ion Chromatography.	.....	.....	D2036–09(A).	
	Ion Selective Electrode.	.....	4500–CN − F–2011	D2036–09(A).	
24. Cyanide-Available, mg/L.	Cyanide Amenable to Chlorination (CATC); Manual distillation with $MgCl_2$, followed by Titrimetric or Spectrophotometric.	.....	4500–CN − G–2011	D2036–09(B).	
	Flow injection and ligand exchange, followed by gas diffusion amperometry [59].	.....	.....	D6888–09	OIA–1677–09. [44]
	Automated Distillation and Colorimetry (no UV digestion).	.....	.....	.....	Kelada–01. [55]
24.A Cyanide-Free, mg/L	Flow Injection, followed by gas diffusion amperometry.	.....	.....	D7237–10	OIA–1677–09. [44]
	Manual micro-diffusion and colorimetry.	.....	.....	D4282–02.	
25. Fluoride—Total, mg/L	Manual distillation [6], followed by any of the following:	.....	4500–F − B–2011.		
	Electrode, manual ..	.....	4500–F − C–2011	D1179–10 (B).	
	Electrode, automated.	.....	.....	.....	I–4327–85. [2]
	Colorimetric, (SPADNS).	.....	4500–F − D–2011	D1179–10 (A).	
	Automated complexone.	.....	4500–F − E–2011.		
	Ion Chromatography.	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2011 or C–2011	D4327–03	993.30. [3]
	CIE/UV	.....	4140 B–2011	D6508–10, D6508, Rev. 2 [54].	
26. Gold—Total, [4] mg/L ...	Digestion [4], followed by any of the following:				
	AA direct aspiration	.....	3111 B–2011.		
	AA furnace	231.2 (Issued 1978) [1].	3113 B–2010.		
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14. [3]
	DCP	.....	.....	.....	See footnote. [34]
27. Hardness—Total, as $CaCO_3$, mg/L.	Automated colorimetric	130.1 (Issued 1971) [1].			
	Titrimetric (EDTA) ..	.....	2340 C–2011	D1126–12	973.52B [3], I–1338–85. [2]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	Ca plus Mg as their carbonates, by any approved method for Ca and Mg (See Parameters 13 and 33), provided that the sum of the lowest point of quantitation for Ca and Mg is below the NPDES permit requirement for Hardness.	.....	2340 B–2011.		
28. Hydrogen ion (pH), pH units.	Electrometric measurement.	.....	4500–H^+ B–2011	D1293–99 (A or B).	973.41 [3], I–1586–85. [2]
	Automated electrode.	150.2 (Dec. 1982) [1].	.....	.....	See footnote [21], I–2587–85. [2]
29. Iridium—Total, [4] mg/L	Digestion [4], followed by any of the following:				
	AA direct aspiration	.....	3111 B–2011.		
	AA furnace	235.2 (Issued 1978) [1].			
	ICP/MS	.....	3125 B–2011.		
30. Iron—Total, [4] mg/L	Digestion [4], followed by any of the following:				
	AA direct aspiration [36].	.....	3111 B–2011 or 3111 C–2011	D1068–10 (A) ..	974.27 [3], I–3381–85. [2]
	AA furnace	.....	3113 B–2010	D1068–10 (B).	
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev. 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14. [3]
	DCP [36]	.....	.....	D4190–08	See footnote. [34]
	Colorimetric (Phenanthroline).	.....	3500–Fe–2011	D1068–10 (C) ..	See footnote. [22]
31. Kjeldahl Nitrogen [5]—Total, (as N), mg/L.	Manual digestion [20] and distillation or gas diffusion, followed by any of the following:	.....	4500–N_{org} B–2011 or C–2011 and 4500–NH_3 B–2011.	D3590–11 (A) ..	I–4515–91. [45]
	Titration	.....	4500–NH_3 C–2011	.....	973.48. [3]
	Nesslerization	.....	.....	D1426–08 (A).	
	Electrode	.....	4500–NH_3 D–2011 or E–2011.	D1426–08 (B).	
	Semi-automated phenate.	350.1, Rev. 2.0 (1993).	4500–NH_3 G–2011 ..... 4500–NH_3 H–2011.		
	Manual phenate, salicylate, or other substituted phenols in Berthelot reaction based methods.	.....	4500–NH_3 F–2011	.....	See footnote. [60]
	Automated Methods for TKN that do not require manual distillation.				
	Automated phenate, salicylate, or other substituted phenols in Berthelot reaction based methods colorimetric (auto digestion and distillation).	351.1 (Rev. 1978) [1].	.....	.....	I–4551–78. [8]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	Semi-automated block digestor colorimetric (distillation not required).	351.2, Rev. 2.0 (1993).	4500–N_{org} D–2011	D3590–11 (B)	I–4515–91 [45]
	Block digester, followed by Auto distillation and Titration.				See footnote. [39]
	Block digester, followed by Auto distillation and Nesslerization.				See footnote. [40]
	Block Digester, followed by Flow injection gas diffusion (distillation not required).				See footnote. [41]
	Digestion with peroxdisulfate, followed by Spectrophotometric (2,6-dimethyl phenol).				Hach 10242. [75]
	Digestion with persulfate, followed by Colorimetric.				NCASI TNTP W10900. [77]
32. Lead—Total, [4] mg/L	Digestion [4], followed by any of the following:				
	AA direct aspiration [36].		3111 B–2011 or 3111 C–2011.	D3559–08 (A or B).	974.27 [3], I–3399–85. [2]
	AA furnace		3113 B–2010	D3559–08 (D)	I–4403–89. [51]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev. 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4471–97. [50]
	DCP [36]			D4190–08	See footnote. [34]
	Voltametry [11]			D3559–08 (C).	
	Colorimetric (Dithizone).		3500–Pb B–2011.		
33. Magnesium—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration		3111 B–2011	D511–09 (B)	974.27 [3], I–3447–85. [2]
	ICP/AES	200.5, Rev. 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14. [3]
	DCP				See footnote. [34]
	Ion Chromatography.			D6919–09.	
34. Manganese—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration [36].		3111 B–2011	D858–12 (A or B).	974.27 [3], I–3454–85. [2]
	AA furnace		3113 B–2010	D858–12 (C).	
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev. 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4471–97. [50]
	DCP [36]			D4190–08	See footnote. [34]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	Colorimetric (Persulfate).	.....	3500–Mn B–2011	.....	920.203. [3]
	Colorimetric (Periodate).	.....	.....	.....	See footnote. [23]
35. Mercury—Total, [4] mg/L.	Cold vapor, Manual	245.1, Rev. 3.0 (1994).	3112 B–2011	D3223–12	977.22 [3], I–3462–85. [2]
	Cold vapor, Automated.	245.2 (Issued 1974) [1].			
	Cold vapor atomic fluorescence spectrometry (CVAFS).	245.7 Rev. 2.0 (2005) [17].	.....	.....	I–4464–01. [71]
	Purge and Trap CVAFS.	1631E [43].			
36. Molybdenum—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration	.....	3111 D–2011	.....	I–3490–85. [2]
	AA furnace	.....	3113 B–2010	.....	I–3492–96. [47]
	ICP/AES [36]	200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4471–97. [50]
	DCP	.....	.....	.....	See footnote. [34]
37. Nickel—Total, [4] mg/L	Digestion [4], followed by any of the following:				
	AA direct aspiration [36].	.....	3111 B–2011 or 3111 C–2011	D1886–08 (A or B).	I–3499–85. [2]
	AA furnace	.....	3113 B–2010	D1886–08 (C) ..	I–4503–89. [51]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev. 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4020–05. [70]
	DCP [36]	.....	.....	D4190–08	See footnote. [34]
38. Nitrate (as N), mg/L ..	Ion Chromatography	300.0, Rev. 2.1 (1993) and 300.1–1, Rev. 1.0 (1997).	4110 B–2011 or C–2011	D4327–03	993.30. [3]
	CIE/UV	.....	4140 B–2011	D6508–10, D6508, Rev. 2 [54].	
	Ion Selective Electrode.	.....	4500–NO_3^- D–2011.		
	Colorimetric (Brucine sulfate).	352.1 (Issued 1971) [1].	.....	.....	973.50 [3], 419D [1,7], p. 28. [9]
	Spectrophotometric (2,6–dimethylphenol).	.....	.....	.....	Hach 10206. [75]
	Nitrate-nitrite N minus Nitrite N (See parameters 39 and 40).	.....	.....	.....	See footnote. [62]
	Enzymatic reduction, followed by automated colorimetric determination.	.....	.....	.....	I–2547–11. [72] I–2548–11. [72] N07–0003. [73]
39. Nitrate-nitrite (as N), mg/L.	Cadmium reduction, Manual.	.....	4500–NO_3^- E–2011	D3867–04 (B).	
	Cadmium reduction, Automated.	353.2, Rev. 2.0 (1993).	4500–NO_3^- F–2011	D3867–04 (A) ..	I–2545–90. [51]
	Automated hydrazine.	.....	4500–NO_3^- H–2011.		
	Reduction/Colorimetric.	.....	.....	.....	See footnote. [62]
	Ion Chromatography.	300.0, Rev. 2.1 (1993) and 300.1–1, Rev. 1.0 (1997).	4110 B–2011 or C–2011	D4327–03	993.30. [3]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	CIE/UV		4140 B–2011	D6508–10	D6508, Rev. 2. [54]
	Enzymatic reduction, followed by automated colorimetric determination.				I–2547–11. [72] I–2548–11. [72] N07–0003. [73]
	Spectrophotometric (2,6-dimethylphenol).				Hach 10206. [75]
40. Nitrite (as N), mg/L	Spectrophotometric: Manual.		4500–NO_2^- B–2011		See footnote. [25]
	Automated (Diazotization).				I–4540–85 [2], See footnote. [62]
	Automated (*bypass cadmium reduction).	353.2, Rev. 2.0 (1993).	4500–NO_3^- F–2011	D3867–04 (A)	I–4545–85. [2]
	Manual (*bypass cadmium reduction).		4500–NO_3^- E–2011	D3867–04 (B).	
	Ion Chromatography.	300.0, Rev. 2.1 (1993) and 300.1–1, Rev. 1.0 (1997).	4110 B–2011 or C–2011	D4327–03	993.30. [3]
	CIE/UV		4140 B–2011	D6508–10, D6508, Rev. 2 [54].	
	Enzymatic reduction, followed by automated colorimetric determination.				I–2547–11. [72] I–2548–11. [72] N07–0003. [73]
41. Oil and grease—Total recoverable, mg/L.	Hexane extractable material (HEM): n-Hexane extraction and gravimetry.	1664 Rev. A; 1664 Rev. B [42].	5520 B–2011 [38].		
	Silica gel treated HEM (SGT–HEM): Silica gel treatment and gravimetry.	1664 Rev. A; 1664 Rev. B [42].	5520 B–2011 [38] and 5520 F–2011 [38].		
42. Organic carbon—Total (TOC), mg/L.	Combustion		5310 B–2011	D7573–09	973.47 [3], p. 14. [24]
	Heated persulfate or UV persulfate oxidation.		5310 C–2011 5310 D–2011	D4839–03	973.47 [3], p. 14. [24]
43. Organic nitrogen (as N), mg/L.	Total Kjeldahl N (Parameter 31) minus ammonia N (Parameter 4).				
44. Ortho-phosphate (as P), mg/L.	Ascorbic acid method:				
	Automated	365.1, Rev. 2.0 (1993).	4500–P F–2011 or G–2011.		973.56 [3], I–4601–85. [2]
	Manual single reagent.		4500–P E–2011	D515–88 (A)	973.55. [3]
	Manual two reagent	365.3 (Issued 1978) [1].			
	Ion Chromatography.	300.0, Rev. 2.1 (1993) and 300.1–1, Rev. 1.0 (1997).	4110 B–2011 or C–2000	D4327–03	993.30. [3]
	CIE/UV		4140 B–2011	D6508–10, D6508, Rev. 2 [54].	
45. Osmium—Total [4], mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration		3111 D–2011.		
	AA furnace	252.2 (Issued 1978) [1].			
46. Oxygen, dissolved, mg/L.	Winkler (Azide modification).		4500–O (B–F)–2011	D888–09 (A)	973.45B [3], I–1575–78. [8]
	Electrode		4500–O G–2011	D888–09 (B)	I–1576–78. [8]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	Luminescence Based Sensor.	.....	.....	D888–09 (C)	See footnote. [63] See footnote. [64]
47. Palladium—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration	.....	3111 B–2011.		
	AA furnace	253.2 (Issued 1978) [1].			
	ICP/MS	.....	3125 B–2011.		
	DCP	.....	.....	.....	See footnote. [34]
48. Phenols, mg/L	Manual distillation [26], followed by any of the following:	420.1 (Rev. 1978) [1].	5530 B–2010	D1783–01.	
	Colorimetric (4AAP) manual.	420.1 (Rev. 1978) [1].	5530 D–2010 [27]	D1783–01 (A or B).	
	Automated colorimetric (4AAP).	420.4 Rev. 1.0 (1993).			
49. Phosphorus (elemental), mg/L.	Gas-liquid chromatography.	.....	.....	.....	See footnote. [28]
50. Phosphorus—Total, mg/L.	Digestion [20], followed by any of the following:	.....	4500–P B(5)–2011	.....	973.55. [3]
	Manual	365.3 (Issued 1978) [1].	4500–P E–2011	D515–88 (A).	
	Automated ascorbic acid reduction.	365.1 Rev. 2.0 (1993).	4500–P (F–H)–2011	.....	973.56 [3], I–4600–85. [2]
	ICP/AES [4, 36]	200.7, Rev. 4.4 (1994).	3120 B–2011	.....	I–4471–97. [50]
	Semi-automated block digestor (TKP digestion).	365.4 (Issued 1974) [1].	.....	D515–88 (B)	I–4610–91. [48]
	Digestion with persulfate, followed by Colorimetric.	.....	.....	.....	NCASI TNTP W10900. [77]
51. Platinum—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration	.....	3111 B–2011.		
	AA furnace	255.2 (Issued 1978) [1].			
	ICP/MS	.....	3125 B–2011.		
	DCP	.....	.....	.....	See footnote. [34]
52. Potassium—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration	.....	3111 B–2011	.....	973.53 [3], I–3630–85. [2]
	ICP/AES	200.7, Rev. 4.4 (1994).	3120 B–2011.		
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14. [3]
	Flame photometric	.....	3500–K B–2011.		
	Electrode	.....	3500–K C–2011.		
	Ion Chromatography.	.....	.....	D6919–09.	
53. Residue—Total, mg/L	Gravimetric, 103–105° ..	.....	2540 B–2011	.....	I–3750–85. [2]
54. Residue—filterable, mg/L.	Gravimetric, 180°	.....	2540 C–2011	D5907–13	I–1750–85. [2]
55. Residue—non-filterable (TSS), mg/L.	Gravimetric, 103–105° post washing of residue.	.....	2540 D–2011	D5907–13	I–3765–85. [2]
56. Residue—settleable, mg/L.	Volumetric, (Imhoff cone), or gravimetric.	.....	2540 F–2011.		
57. Residue—Volatile, mg/L.	Gravimetric, 550°	160.4 (Issued 1971) [1].	2540–E–2011	.....	I–3753–85. [2]
58. Rhodium—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration, or.	.....	3111 B–2011.		
	AA furnace	265.2 (Issued 1978) [1].			
	ICP/MS	.....	3125 B–2011.		
59. Ruthenium—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration, or.	.....	3111 B–2011.		

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	AA furnace	267.2 [1].			
	ICP/MS		3125 B–2011.		
60. Selenium—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA furnace		3113 B–2010	D3859–08 (B)	I–4668–98. [49]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12.	
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4020–05. [70]
	AA gaseous hydride		3114 B–2011, or 3114 C–2011.	D3859–08 (A)	I–3667–85. [2]
61. Silica—Dissolved, [37] mg/L.	0.45-micron filtration followed by any of the following:				
	Colorimetric, Manual.		4500–SiO_2 C–2011	D859–10	I–1700–85. [2]
	Automated (Molybdosilicate).		4500–SiO_2 E–2011 or F–2011.		I–2700–85. [2]
	ICP/AES	200.5, Rev. 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011		I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14. [3]
62. Silver—Total, [4] [31] mg/L	Digestion [4, 29], followed by any of the following:				
	AA direct aspiration		3111 B–2011 or 3111 C–2011		974.27 [3], p. 37 [9], I–3720–85. [2]
	AA furnace		3113 B–2010		I–4724–89. [51]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES	200.5, Rev. 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4471–97. [50]
	DCP				See footnote. [34]
63. Sodium—Total, [4] mg/L	Digestion [4], followed by any of the following:				
	AA direct aspiration		3111 B–2011		973.54 [3], I–3735–85. [2]
	ICP/AES	200.5, Rev. 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011		I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14. [3]
	DCP				See footnote. [34]
	Flame photometric		3500–Na B–2011.		
	Ion Chromatography.			D6919–09.	
64. Specific conductance, micromhos/cm at 25 °C.	Wheatstone bridge	120.1 (Rev. 1982) [1].	2510 B–2011	D1125–95(99) (A).	973.40 [3], I–2781–85. [2]
65. Sulfate (as SO_4), mg/L.	Automated colorimetric	375.2, Rev. 2.0 (1993).	4500–SO_4^{2-} F–2011 or G–2011.		
	Gravimetric		4500–SO_4^{2-} C–2011 or D–2011.		925.54. [3]
	Turbidimetric		4500–SO_4^{2-} E–2011	D516–11.	
	Ion Chromatography.	300.0, Rev. 2.1 (1993) and 300.1–1, Rev. 1.0 (1997).	4110 B–2011 or C–2011	D4327–03	993.30 [3], I–4020–05. [70]
	CIE/UV		4140 B–2011	D6508–1010	D6508, Rev. 2. [54]
66. Sulfide (as S), mg/L	Sample Pretreatment		4500–S^{2-}>B, C–2011.		
	Titrimetric (iodine)		4500–S^{2-} F–2011		I–3840–85. [2]
	Colorimetric (methylene blue).		4500–S^{2-} D–2011.		

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	Ion Selective Electrode.	.....	4500–S^{2-} G–2011	D4658–09.	
67. Sulfite (as SO_3), mg/L	Titrimetric (iodine-iodate)	.....	4500–SO_3^{2-} B–2011.		
68. Surfactants, mg/L	Colorimetric (methylene blue).	.....	5540 C–2011	D2330–02.	
69. Temperature, °C	Thermometric	.....	2550 B–2010	.....	See footnote. [32]
70. Thallium—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration	.....	3111 B–2011.		
	AA furnace	279.2 (Issued 1978) [1].	3113 B–2010.		
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES	200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12.	
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4471–97. [50]
71. Tin—Total, [4] mg/L	Digestion [4], followed by any of the following:				
	AA direct aspiration	.....	3111 B–2011	.....	I–3850–78. [8]
	AA furnace	.....	3113 B–2010.		
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES	200.5, Rev. 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).			
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14. [3]
72. Titanium—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration	.....	3111 D–2011.		
	AA furnace	283.2 (Issued 1978) [1].			
	ICP/AES	200.7, Rev. 4.4 (1994).			
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14. [3]
	DCP	.....	.....	.....	See footnote. [34]
73. Turbidity, NTU [53]	Nephelometric	180.1, Rev. 2.0 (1993).	2130 B–2011	D1889–00	I–3860–85. [2] See footnote. [65] See footnote. [66] See footnote. [67]
74. Vanadium—Total, [4] mg/L.	Digestion [4], followed by any of the following:				
	AA direct aspiration	.....	3111 D–2011.		
	AA furnace	.....	3113 B–2010	D3373–12.	
	ICP/AES	200.5, Rev. 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4020–05. [70]
	DCP	.....	.....	D4190–08	See footnote. [34]
	Colorimetric (Gallic Acid).	.....	3500–V B–2011.		
75. Zinc—Total [4], mg/L	Digestion [4], followed by any of the following:				
	AA direct aspiration [36].	.....	3111 B–2011 or 3111 C–2011.	D1691–12 (A or B).	974.27 [3], p. 37 [9], I–3900–85. [2]
	AA furnace	289.2 (Issued 1978) [1].			
	ICP/AES [36]	200.5, Rev. 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97. [50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2011	D5673–10	993.14 [3], I–4020–05 [70]
	DCP [36]	.....	.....	D4190–08	See footnote. [34]
	Colorimetric (Zincon).	.....	3500 Zn B–2011	.....	See footnote. [33]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
76. Acid Mine Drainage ...	.....	1627 [69].			

Table IB Notes:

[1] Methods for Chemical Analysis of Water and Wastes, EPA–600/4–79–020. Revised March 1983 and 1979, where applicable. U.S. EPA.

[2] Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments, Techniques of Water-Resource Investigations of the U.S. Geological Survey, Book 5, Chapter A1., unless otherwise stated. 1989. USGS.

[3] Official Methods of Analysis of the Association of Official Analytical Chemists, Methods Manual, Sixteenth Edition, 4th Revision, 1998. AOAC International.

[4] For the determination of total metals (which are equivalent to total recoverable metals) the sample is not filtered before processing. A digestion procedure is required to solubilize analytes in suspended material and to break down organic-metal complexes (to convert the analyte to a detectable form for colorimetric analysis). For non-platform graphite furnace atomic absorption determinations a digestion using nitric acid (as specified in Section 4.1.3 of Methods for the Chemical Analysis of Water and Wastes) is required prior to analysis. The procedure used should subject the sample to gentle, acid refluxing and at no time should the sample be taken to dryness. For direct aspiration flame atomic absorption determinations (FLAA) a combination acid (nitric and hydrochloric acids) digestion is preferred prior to analysis. The approved total recoverable digestion is described as Method 200.2 in Supplement I of ''Methods for the Determination of Metals in Environmental Samples'' EPA/600R–94/111, May, 1994, and is reproduced in EPA Methods 200.7, 200.8, and 200.9 from the same Supplement. However, when using the gaseous hydride technique or for the determination of certain elements such as antimony, arsenic, selenium, silver, and tin by non-EPA graphite furnace atomic absorption methods, mercury by cold vapor atomic absorption, the noble metals and titanium by FLAA, a specific or modified sample digestion procedure may be required and in all cases the referenced method write-up should be consulted for specific instruction and/or cautions. For analyses using inductively coupled plasma-atomic emission spectrometry (ICP–AES), the direct current plasma (DCP) technique or EPA spectrochemical techniques (platform furnace AA, ICP–AES, and ICP–MS) use EPA Method 200.2 or an approved alternate procedure (*e.g.,* CEM microwave digestion, which may be used with certain analytes as indicated in Table IB); the total recoverable digestion procedures in EPA Methods 200.7, 200.8, and 200.9 may be used for those respective methods. Regardless of the digestion procedure, the results of the analysis after digestion procedure are reported as ''total'' metals.

[5] Copper sulfate or other catalysts that have been found suitable may be used in place of mercuric sulfate.

[6] Manual distillation is not required if comparability data on representative effluent samples are on file to show that this preliminary distillation step is not necessary: however, manual distillation will be required to resolve any controversies. In general, the analytical method should be consulted regarding the need for distillation. If the method is not clear, the laboratory may compare a minimum of 9 different sample matrices to evaluate the need for distillation. For each matrix, a matrix spike and matrix spike duplicate are analyzed both with and without the distillation step. (A total of 36 samples, assuming 9 matrices). If results are comparable, the laboratory may dispense with the distillation step for future analysis. Comparable is defined as < 20% RPD for all tested matrices). Alternatively the two populations of spike recovery percentages may be compared using a recognized statistical test.

[7] Industrial Method Number 379–75 WE Ammonia, Automated Electrode Method, Technicon Auto Analyzer II. February 19, 1976. Bran & Luebbe Analyzing Technologies Inc.

[8] The approved method is that cited in Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A1. 1979. USGS.

[9] American National Standard on Photographic Processing Effluents. April 2, 1975. American National Standards Institute.

[10] In-Situ Method 1003–8–2009, Biochemical Oxygen Demand (BOD) Measurement by Optical Probe. 2009. In-Situ Incorporated.

[11] The use of normal and differential pulse voltage ramps to increase sensitivity and resolution is acceptable.

[12] Carbonaceous biochemical oxygen demand ($CBOD_5$) must not be confused with the traditional BOD_5 test method which measures ''total BOD.'' The addition of the nitrification inhibitor is not a procedural option, but must be included to report the $CBOD_5$ parameter. A discharger whose permit requires reporting the traditional BOD_5 may not use a nitrification inhibitor in the procedure for reporting the results. Only when a discharger's permit specifically states $CBOD_5$ is required can the permittee report data using a nitrification inhibitor.

[13] OIC Chemical Oxygen Demand Method. 1978. Oceanography International Corporation.

[14] Method 8000, Chemical Oxygen Demand, Hach Handbook of Water Analysis, 1979. Hach Company.

[15] The back titration method will be used to resolve controversy.

[16] Orion Research Instruction Manual, Residual Chlorine Electrode Model 97–70. 1977. Orion Research Incorporated. The calibration graph for the Orion residual chlorine method must be derived using a reagent blank and three standard solutions, containing 0.2, 1.0, and 5.0 mL 0.00281 N potassium iodate/100 mL solution, respectively.

[17] Method 245.7, Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry, EPA–821–R–05–001. Revision 2.0, February 2005. US EPA.

[18] National Council of the Paper Industry for Air and Stream Improvement (NCASI) Technical Bulletin 803, May 2000.

[19] Method 8506, Biocinchoninate Method for Copper, Hach Handbook of Water Analysis. 1979. Hach Company.

[20] When using a method with block digestion, this treatment is not required.

[21] Industrial Method Number 378–75WA, Hydrogen ion (pH) Automated Electrode Method, Bran & Luebbe (Technicon) Autoanalyzer II. October 1976. Bran & Luebbe Analyzing Technologies.

[22] Method 8008, 1,10-Phenanthroline Method using FerroVer Iron Reagent for Water. 1980. Hach Company.

[23] Method 8034, Periodate Oxidation Method for Manganese, Hach Handbook of Wastewater Analysis. 1979. Hach Company.

[24] Methods for Analysis of Organic Substances in Water and Fluvial Sediments, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A3, (1972 Revised 1987). 1987. USGS.

[25] Method 8507, Nitrogen, Nitrite-Low Range, Diazotization Method for Water and Wastewater. 1979. Hach Company.

[26] Just prior to distillation, adjust the sulfuric-acid-preserved sample to pH 4 with 1 + 9 NaOH.

[27] The colorimetric reaction must be conducted at a pH of 10.0 ± 0.2.

[28] Addison, R.F., and R.G. Ackman. 1970. Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography, *Journal of Chromatography*, 47(3):421–426.

[29] Approved methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/L and above are inadequate where silver exists as an inorganic halide. Silver halides such as the bromide and chloride are relatively insoluble in reagents such as nitric acid but are readily soluble in an aqueous buffer of sodium thiosulfate and sodium hydroxide to pH of 12. Therefore, for levels of silver above 1 mg/L, 20 mL of sample should be diluted to 100 mL by adding 40 mL each of 2 M $Na_2S_2O_3$ and NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/L the approved method is satisfactory.

[30] The use of EDTA decreases method sensitivity. Analysts may omit EDTA or replace with another suitable complexing reagent provided that all method specified quality control acceptance criteria are met.

[31] For samples known or suspected to contain high levels of silver (*e.g.,* in excess of 4 mg/L), cyanogen iodide should be used to keep the silver in solution for analysis. Prepare a cyanogen iodide solution by adding 4.0 mL of concentrated NH_4OH, 6.5 g of KCN, and 5.0 mL of a 1.0 N solution of I_2 to 50 mL of reagent water in a volumetric flask and dilute to 100.0 mL. After digestion of the sample, adjust the pH of the digestate to >7 to prevent the formation of HCN under acidic conditions. Add 1 mL of the cyanogen iodide solution to the sample digestate and adjust the volume to 100 mL with reagent water (NOT acid). If cyanogen iodide is added to sample digestates, then silver standards must be prepared that contain cyanogen iodide as well. Prepare working standards by diluting a small volume of a silver stock solution with water and adjusting the pH>7 with NH_4OH. Add 1 mL of the cyanogen iodide solution and let stand 1 hour. Transfer to a 100-mL volumetric flask and dilute to volume with water.

[32] ''Water Temperature-Influential Factors, Field Measurement and Data Presentation,'' Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 1, Chapter D1. 1975. USGS.

[33] Method 8009, Zincon Method for Zinc, Hach Handbook of Water Analysis, 1979. Hach Company.

[34] Method AES0029, Direct Current Plasma (DCP) Optical Emission Spectrometric Method for Trace Elemental Analysis of Water and Wastes. 1986—Revised 1991. Thermo Jarrell Ash Corporation.

[35] In-Situ Method 1004–8–2009, Carbonaceous Biochemical Oxygen Demand (CBOD) Measurement by Optical Probe. 2009. In-Situ Incorporated.

[36] Microwave-assisted digestion may be employed for this metal, when analyzed by this methodology. Closed Vessel Microwave Digestion of Wastewater Samples for Determination of Metals. April 16, 1992. CEM Corporation

[37] When determining boron and silica, only plastic, PTFE, or quartz laboratory ware may be used from start until completion of analysis.

[38] Only use n-hexane (n-Hexane—85% minimum purity, 99.0% min. saturated C6 isomers, residue less than 1 mg/L) extraction solvent when determining Oil and Grease parameters—Hexane Extractable Material (HEM), or Silica Gel Treated HEM (analogous to EPA Methods 1664 Rev. A and 1664 Rev. B). Use of other extraction solvents is prohibited.

[39] Method PAI–DK01, Nitrogen, Total Kjeldahl, Block Digestion, Steam Distillation, Titrimetric Detection. Revised December 22, 1994. OI Analytical.

[40] Method PAI–DK02, Nitrogen, Total Kjeldahl, Block Digestion, Steam Distillation, Colorimetric Detection. Revised December 22, 1994. OI Analytical.

[41] Method PAI–DK03, Nitrogen, Total Kjeldahl, Block Digestion, Automated FIA Gas Diffusion. Revised December 22, 1994. OI Analytical.

[42] Method 1664 Rev. B is the revised version of EPA Method 1664 Rev. A. U.S. EPA. February 1999, Revision A. Method 1664, n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT–HEM; Non-polar Material) by Extraction and Gravimetry. EPA–821–R–98–002. U.S. EPA. February 2010, Revision B. Method 1664, n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT–HEM; Non-polar Material) by Extraction and Gravimetry. EPA–821–R–10–001.

[43] Method 1631, Revision E, Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, EPA–821–R–02–019. Revision E. August 2002, U.S. EPA. The application of clean techniques described in EPA's Method 1669: *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels,* EPA–821–R–96–011, are recommended to preclude contamination at low-level, trace metal determinations.

[44] Method OIA–1677–09, Available Cyanide by Ligand Exchange and Flow Injection Analysis (FIA). 2010. OI Analytical.

[45] Open File Report 00–170, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Ammonium Plus Organic Nitrogen by a Kjeldahl Digestion Method and an Automated Photometric Finish that Includes Digest Cleanup by Gas Diffusion. 2000. USGS.

[46] Open File Report 93–449, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Chromium in Water by Graphite Furnace Atomic Absorption Spectrophotometry. 1993. USGS.

[47] Open File Report 97–198, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Molybdenum by Graphite Furnace Atomic Absorption Spectrophotometry. 1997. USGS.

[48] Open File Report 92–146, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Total Phosphorus by Kjeldahl Digestion Method and an Automated Colorimetric Finish That Includes Dialysis. 1992. USGS.

[49] Open File Report 98–639, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Arsenic and Selenium in Water and Sediment by Graphite Furnace-Atomic Absorption Spectrometry. 1999. USGS.

[50] Open File Report 98–165, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Elements in Whole-water Digests Using Inductively Coupled Plasma-Optical Emission Spectrometry and Inductively Coupled Plasma-Mass Spectrometry. 1998. USGS.

[51] Open File Report 93–125, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments. 1993. USGS.

[52] Unless otherwise indicated, all EPA methods, excluding EPA Method 300.1–1, are published in U.S. EPA. May 1994. Methods for the Determination of Metals in Environmental Samples, Supplement I, EPA/600/R–94/111; or U.S. EPA. August 1993. Methods for the Determination of Inorganic Substances in Environmental Samples, EPA/600/R–93/100. EPA Method 300.1 is US EPA. Revision 1.0, 1997, including errata cover sheet April 27, 1999. Determination of Inorganic Ions in Drinking Water by Ion Chromatography.

[53] Styrene divinyl benzene beads (*e.g.,* AMCO–AEPA–1 or equivalent) and stabilized formazin (*e.g.,* Hach StablCal™ or equivalent) are acceptable substitutes for formazin.

[54] Method D6508–10, Test Method for Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis and Chromate Electrolyte. 2010. ASTM.

[55] Kelada-01, Kelada Automated Test Methods for Total Cyanide, Acid Dissociable Cyanide, and Thiocyanate, EPA 821–B–01–009, Revision 1.2, August 2001. US EPA. Note: A 450–W UV lamp may be used in this method instead of the 550–W lamp specified if it provides performance within the quality control (QC) acceptance criteria of the method in a given instrument. Similarly, modified flow cell configurations and flow conditions may be used in the method, provided that the QC acceptance criteria are met.

[56] QuikChem Method 10–204–00–1–X, Digestion and Distillation of Total Cyanide in Drinking and Wastewaters using MICRO DIST and Determination of Cyanide by Flow Injection Analysis. Revision 2.2, March 2005. Lachat Instruments.

[57] When using sulfide removal test procedures described in EPA Method 335.4–1, reconstitute particulate that is filtered with the sample prior to distillation.

[58] Unless otherwise stated, if the language of this table specifies a sample digestion and/or distillation ''followed by'' analysis with a method, approved digestion and/or distillation are required prior to analysis.

[59] Samples analyzed for available cyanide using OI Analytical method OIA–1677–09 or ASTM method D6888–09 that contain particulate matter may be filtered only after the ligand exchange reagents have been added to the samples, because the ligand exchange process converts complexes containing available cyanide to free cyanide, which is not removed by filtration. Analysts are further cautioned to limit the time between the addition of the ligand exchange reagents and sample filtration to no more than 30 minutes to preclude settling of materials in samples.

[60] Analysts should be aware that pH optima and chromophore absorption maxima might differ when phenol is replaced by a substituted phenol as the color reagent in Berthelot Reaction (''phenol-hypochlorite reaction'') colorimetric ammonium determination methods. For example when phenol is used as the color reagent, pH optimum and wavelength of maximum absorbance are about 11.5 and 635 nm, respectively—see, Patton, C.J. and S.R. Crouch. March 1977. Anal. Chem. 49:464–469. These reaction parameters increase to pH > 12.6 and 665 nm when salicylate is used as the color reagent—see, Krom, M.D. April 1980. The Analyst 105:305–316.

[61] If atomic absorption or ICP instrumentation is not available, the aluminon colorimetric method detailed in the 19th Edition of *Standard Methods* may be used. This method has poorer precision and bias than the methods of choice.

[62] Easy (1-Reagent) Nitrate Method, Revision November 12, 2011. Craig Chinchilla.

[63] Hach Method 10360, Luminescence Measurement of Dissolved Oxygen in Water and Wastewater and for Use in the Determination of BOD_5 and $cBOD_5$. Revision 1.2, October 2011. Hach Company. This method may be used to measure dissolved oxygen when performing the methods approved in Table IB for measurement of biochemical oxygen demand (BOD) and carbonaceous biochemical oxygen demand (CBOD).

[64] In-Situ Method 1002–8–2009, Dissolved Oxygen (DO) Measurement by Optical Probe. 2009. In-Situ Incorporated.

[65] Mitchell Method M5331, Determination of Turbidity by Nephelometry. Revision 1.0, July 31, 2008. Leck Mitchell.

[66] Mitchell Method M5271, Determination of Turbidity by Nephelometry. Revision 1.0, July 31, 2008. Leck Mitchell.

[67] Orion Method AQ4500, Determination of Turbidity by Nephelometry. Revision 5, March 12, 2009. Thermo Scientific.

[68] EPA Method 200.5, Determination of Trace Elements in Drinking Water by Axially Viewed Inductively Coupled Plasma-Atomic Emission Spectrometry, EPA/600/R–06/115. Revision 4.2, October 2003. US EPA.

[69] Method 1627, Kinetic Test Method for the Prediction of Mine Drainage Quality, EPA–821–R–09–002. December 2011. US EPA.

[70] Techniques and Methods Book 5–B1, Determination of Elements in Natural-Water, Biota, Sediment and Soil Samples Using Collision/Reaction Cell Inductively Coupled Plasma-Mass Spectrometry, Chapter 1, Section B, Methods of the National Water Quality Laboratory, Book 5, Laboratory Analysis, 2006. USGS.

[71] Water-Resources Investigations Report 01–4132, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Organic Plus Inorganic Mercury in Filtered and Unfiltered Natural Water with Cold Vapor-Atomic Fluorescence Spectrometry, 2001. USGS.

[72] USGS Techniques and Methods 5–B8, Chapter 8, Section B, Methods of the National Water Quality Laboratory Book 5, Laboratory Analysis, 2011 USGS.

[73] NECi Method N07–0003, Revision 9.0, March 2014, Method for Nitrate Reductase Nitrate-Nitrogen Analysis, The Nitrate Elimination Co., Inc.

[74] Timberline Instruments, LLC Method Ammonia-001, Timberline Instruments, LLC.

[75] Hach Company Method 10206, Hach Company.

[76] Hach Company Method 10242, Hach Company.

[77] National Council for Air and Stream Improvement (NCASI) Method TNTP–W10900, Total (Kjeldahl) Nitrogen and Total Phosphorus in Pulp and Paper Biologically Treated Effluent by Alkaline Persulfate Digestion. June 2011.

TABLE IC—LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS

Parameter [1]	Method	EPA [2 7]	Standard methods	ASTM	Other
1. Acenaphthene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
2. Acenaphthylene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
3. Acrolein	GC	603			
	GC/MS	624.1 [4],1624B			
4. Acrylonitrile	GC	603			
	GC/MS	624.1 [4],1624B			
5. Anthracene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440B–2005	D4657–92 (98)	
6. Benzene	GC	602	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
7. Benzidine	Spectro-photo-metric.				See footnote [3], p.1.
	GC/MS	625.1 [5], 1625B	6410 B–2000		
	HPLC	605			
8. Benzo(a)anthracene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
9. Benzo(a)pyrene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
10. Benzo(b)fluoranthene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
11. Benzo(g,h,i)perylene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
12. Benzo(k)fluoranthene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
13. Benzyl chloride	GC				See footnote [3], p. 130.
	GC/MS				See footnote [6], p. S102.
14. Butyl benzyl phthalate	GC	606			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
15. bis(2-Chloroethoxy) methane	GC	611			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
16. bis(2-Chloroethyl) ether	GC	611			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
17. bis(2-Ethylhexyl) phthalate	GC	606			

TABLE IC—LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS—Continued

Parameter [1]	Method	EPA [2 7]	Standard methods	ASTM	Other
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
18. Bromodichloromethane	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
19. Bromoform	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
20. Bromomethane	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
21. 4-Bromophenyl phenyl ether	GC	611			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
22. Carbon tetrachloride	GC	601	6200 C–2011		See footnote [3], p. 130.
	GC/MS	624.1, 1624B	6200 B–2011		
23. 4-Chloro-3-methyl phenol	GC	604	6420 B–2000		
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
24. Chlorobenzene	GC	601, 602	6200 C–2011		See footnote [3], p. 130.
	GC/MS	624.1, 1624B	6200 B–2011		
25. Chloroethane	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
26. 2-Chloroethylvinyl ether	GC	601			
	GC/MS	624.1, 1624B			
27. Chloroform	GC	601	6200 C–2011		See footnote [3], p. 130.
	GC/MS	624.1, 1624B	6200 B–2011		
28. Chloromethane	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
29. 2-Chloronaphthalene	GC	612			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
30. 2-Chlorophenol	GC	604	6420 B–2000		
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
31. 4-Chlorophenyl phenyl ether	GC	611			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
32. Chrysene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
33. Dibenzo(a,h)anthracene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
34. Dibromochloromethane	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
35. 1,2-Dichlorobenzene	GC	601, 602	6200 C–2011		
	GC/MS	625.1, 1625B	6200 B–2011		See footnote [9], p. 27.
36. 1,3-Dichlorobenzene	GC	601, 602	6200 C–2011		
	GC/MS	624.1, 1625B	6200 B–2011		See footnote [9], p. 27.
37. 1,4-Dichlorobenzene	GC	601, 602	6200 C–2011		
	GC/MS	624.1, 1625B	6200 B–2011		See footnote [9], p. 27.
38. 3,3′-Dichlorobenzidine	GC/MS	625.1, 1625B	6410 B–2000		
	HPLC	605			
39. Dichlorodifluoromethane	GC	601			
	GC/MS		6200 C–2011		
40. 1,1-Dichloroethane	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
41. 1,2-Dichloroethane	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
42. 1,1-Dichloroethene	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
43. trans-1,2-Dichloroethene	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
44. 2,4-Dichlorophenol	GC	604	6420 B–2000		

TABLE IC—LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS—Continued

Parameter [1]	Method	EPA [2 7]	Standard methods	ASTM	Other
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
45. 1,2-Dichloropropane	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
46. cis-1,3-Dichloropropene	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
47. trans-1,3-Dichloropropene	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
48. Diethyl phthalate	GC	606			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
49. 2,4-Dimethylphenol	GC	604	6420 B–2000		
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
50. Dimethyl phthalate	GC	606			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
51. Di-n-butyl phthalate	GC	606			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
52. Di-n-octyl phthalate	GC	606			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
53. 2, 4-Dinitrophenol	GC	604	6420 B–2000		See footnote [9], p. 27.
	GC/MS	625.1, 1625B	6410 B–2000		
54. 2,4-Dinitrotoluene	GC	609			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
55. 2,6-Dinitrotoluene	GC	609			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
56. Epichlorohydrin	GC				See footnote [3], p. 130.
	GC/MS				See footnote [6], p. S102.
57. Ethylbenzene	GC	602	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
58. Fluoranthene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
59. Fluorene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
60. 1,2,3,4,6,7,8-Heptachloro-dibenzofuran	GC/MS	1613B			
61. 1,2,3,4,7,8,9-Heptachloro-dibenzofuran	GC/MS	1613B			
62. 1,2,3,4,6,7,8- Heptachloro-dibenzo-*p*-dioxin	GC/MS	1613B			
63. Hexachlorobenzene	GC	612			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
64. Hexachlorobutadiene	GC	612			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
65. Hexachlorocyclopentadiene	GC	612			
	GC/MS	625.1 [5], 1625B	6410 B–2000		See footnote [9], p. 27.
66. 1,2,3,4,7,8-Hexachloro-dibenzofuran	GC/MS	1613B			
67. 1,2,3,6,7,8-Hexachloro-dibenzofuran	GC/MS	1613B			
68. 1,2,3,7,8,9-Hexachloro-dibenzofuran	GC/MS	1613B			
69. 2,3,4,6,7,8-Hexachloro-dibenzofuran	GC/MS	1613B			
70. 1,2,3,4,7,8-Hexachloro-dibenzo-*p*-dioxin	GC/MS	1613B			
71. 1,2,3,6,7,8-Hexachloro-dibenzo-*p*-dioxin	GC/MS	1613B			
72. 1,2,3,7,8,9-Hexachloro-dibenzo-*p*-dioxin	GC/MS	1613B			
73. Hexachloroethane	GC	612			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
74. Indeno(1,2,3-c,d) pyrene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.

TABLE IC—LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS—Continued

Parameter [1]	Method	EPA [2 7]	Standard methods	ASTM	Other
	HPLC	610	6440 B–2005	D4657–92 (98)	
75. Isophorone	GC	609			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
76. Methylene chloride	GC	601	6200 C–2011		See footnote [3], p. 130.
	GC/MS	624.1, 1624B	6200 B–2011		
77. 2-Methyl-4,6-dinitrophenol	GC	604	6420 B–2000		
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
78. Naphthalene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2005		
79. Nitrobenzene	GC	609			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC			D4657–92 (98)	
80. 2-Nitrophenol	GC	604	6420 B–2000		
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
81. 4-Nitrophenol	GC	604	6420 B–2000		
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
82. N-Nitrosodimethylamine	GC	607			
	GC/MS	625.1 [5], 1625B	6410 B–2000		See footnote [9], p. 27.
83. N-Nitrosodi-n-propylamine	GC	607			
	GC/MS	625.1 [5], 1625B	6410 B–2000		See footnote [9], p. 27.
84. N-Nitrosodiphenylamine	GC	607			
	GC/MS	625.1 [5], 1625B	6410 B–2000		See footnote [9], p. 27.
85. Octachlorodibenzofuran	GC/MS	1613B [10]			
86. Octachlorodibenzo-*p*-dioxin	GC/MS	1613B [10]			
87. 2,2′-oxybis(1-chloropropane) [12] [also known as bis(2-Chloro-1-methylethyl) ether].	GC	611			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
88. PCB–1016	GC	608.3			See footnote [3], p. 43; See footnote. [8]
	GC/MS	625.1	6410 B–2000		
89. PCB–1221	GC	608.3			See footnote [3], p. 43; See footnote. [8]
	GC/MS	625.1	6410 B–2000		
90. PCB–1232	GC	608.3			See footnote [3], p. 43; See footnote. [8]
	GC/MS	625.1	6410 B–2000		
91. PCB–1242	GC	608.3			See footnote [3], p. 43; See footnote. [8]
	GC/MS	625.1	6410 B–2000		
92. PCB–1248	GC	608.3			See footnote [3], p. 43; See footnote. [8]
	GC/MS	625.1	6410 B–2000		
93. PCB–1254	GC	608.3			See footnote [3], p. 43; See footnote. [8]
	GC/MS	625.1	6410 B–2000		
94. PCB–1260	GC	608.3			See footnote [3], p. 43; See footnote. [8]
	GC/MS	625.1	6410 B–2000		
95. 1,2,3,7,8-Pentachloro-dibenzofuran	GC/MS	1613B			
96. 2,3,4,7,8-Pentachloro-dibenzofuran	GC/MS	1613B			
97. 1,2,3,7,8,-Pentachloro-dibenzo-*p*-dioxin	GC/MS	1613B			

TABLE IC—LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS—Continued

Parameter [1]	Method	EPA [2 7]	Standard methods	ASTM	Other
98. Pentachlorophenol	GC	604	6420 B–2000		See footnote [3], p. 140.
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
99. Phenanthrene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98)	
100. Phenol	GC	604	6420 B–2000		
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
101. Pyrene	GC	610			
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2005	D4657–92 (98).	
102. 2,3,7,8-Tetrachloro-dibenzofuran	GC/MS	1613B [10]			
103. 2,3,7,8-Tetrachloro-dibenzo-*p*-dioxin	GC/MS	613, 625.1 [5a], 1613B			
104. 1,1,2,2-Tetrachloroethane	GC	601	6200 C–2011		See footnote [3], p. 130.
	GC/MS	624.1, 1624B	6200 B–2011		
105. Tetrachloroethene	GC	601	6200 C–2011		See footnote [3], p. 130.
	GC/MS	624.1, 1624B	6200 B–2011		
106. Toluene	GC	602	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
107. 1,2,4-Trichlorobenzene	GC	612			See footnote [3], p. 130.
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
108. 1,1,1-Trichloroethane	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
109. 1,1,2-Trichloroethane	GC	601	6200 C–2011		See footnote [3], p. 130.
	GC/MS	624.1, 1624B	6200 B–2011		
110. Trichloroethene	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
111. Trichlorofluoromethane	GC	601	6200 C–2011		
	GC/MS	624.1	6200 B–2011		
112. 2,4,6-Trichlorophenol	GC	604	6420 B–2000		
	GC/MS	625.1, 1625B	6410 B–2000		See footnote [9], p. 27.
113. Vinyl chloride	GC	601	6200 C–2011		
	GC/MS	624.1, 1624B	6200 B–2011		
114. Nonylphenol	GC/MS			D7065–11	
115. Bisphenol A (BPA)	GC/MS			D7065–11	
116. p-tert-Octylphenol (OP)	GC/MS			D7065–11	
117. Nonylphenol Monoethoxylate (NP1EO)	GC/MS			D7065–11	
118. Nonylphenol Diethoxylate (NP2EO)	GC/MS			D7065–11	
119. Adsorbable Organic Halides (AOX)	Adsorption and Coulometric Titration.	1650 [11]			
120. Chlorinated Phenolics	In Situ Acetylation and GC/MS.	1653 [11]			

Table IC notes:

[1] All parameters are expressed in micrograms per liter (μg/L) except for Method 1613B, in which the parameters are expressed in picograms per liter (pg/L).

[2] The full text of Methods 601–613, 1613B, 1624B, and 1625B are provided at Appendix A, Test Procedures for Analysis of Organic Pollutants, of this Part 136. The standardized test procedure to be used to determine the method detection limit (MDL) for these test procedures is given at Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, of this Part 136. Methods 608.3, 624.1, and 625.1 are available at: *water.epa.gov/scitech/methods/cwa/methods_index.cfm.*

[3] Methods for Benzidine: Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater. September 1978. U.S. EPA.

[4] Method 624.1 may be used for quantitative determination of acrolein and acrylonitrile, provided that the laboratory has documentation to substantiate the ability to detect and quantify these analytes at levels necessary to comply with any associated regulations. In addition, the use of sample introduction techniques other than simple purge-and-trap may be required. QC acceptance criteria from Method 603 should be used when analyzing samples for acrolein and acrylonitrile in the absence of such criteria in Method 624.1.

[5] Method 625.1 may be extended to include benzidine, hexachlorocyclopentadiene, N-nitrosodimethylamine, N-nitrosodi-n-propylamine, and N-nitrosodiphenylamine. However, when they are known to be present, Methods 605, 607, and 612, or Method 1625B, are preferred methods for these compounds.

[5a] Method 625.1 screening only.

[6] Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency, Supplement to the 15th Edition of *Standard Methods for the Examination of Water and Wastewater* 1981. American Public Health Association (APHA).

[7] Each analyst must make an initial, one-time demonstration of their ability to generate acceptable precision and accuracy with Methods 601–603, 1624B, and 1625B in accordance with procedures each in Section 8.2 of each of these Methods. Additionally, each laboratory, on an ongoing basis must spike and analyze 10% (5% for Methods 624.1 and 625.1 and 100% for methods 1624B and 1625B) of all samples to monitor and evaluate laboratory data quality in accordance with Sections 8.3 and 8.4 of these methods. When the recovery of any parameter falls outside the warning limits, the analytical results for that parameter in the unspiked sample are suspect. The results should be reported, but cannot be used to demonstrate regulatory compliance. These quality control requirements also apply to the Standard Methods, ASTM Methods, and other methods cited.

[8] Organochlorine Pesticides and PCBs in Wastewater Using Empore™ Disk. Revised October 28, 1994. 3M Corporation.

[9] Method O–3116–87 is in Open File Report 93–125, Methods of Analysis by U.S. Geological Survey National Water Quality Laboratory—Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments. 1993. USGS.

[10] Analysts may use Fluid Management Systems, Inc. Power-Prep system in place of manual cleanup provided the analyst meets the requirements of Method 1613B (as specified in Section 9 of the method) and permitting authorities. Method 1613, Revision B, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. Revision B, 1994. U.S. EPA. The full text of this method is provided in Appendix A to 40 CFR part 136 and at *http://water.epa.gov/scitech/methods/cwa/index.cfm.*

[11] Method 1650, Adsorbable Organic Halides by Adsorption and Coulometric Titration. Revision C, 1997 U.S. EPA. Method 1653, Chlorinated Phenolics in Wastewater by In Situ Acetylation and GCMS. Revision A, 1997 U.S. EPA. The full text for both of these methods is provided at Appendix A in part 430, The Pulp, Paper, and Paperboard Point Source Category.

[12] The compound was formerly inaccurately labeled as 2,2′-oxybis(2-chloropropane) and bis(2-chloroisopropyl) ether. Some versions of Methods 611, and 1625 inaccurately list the analyte as ''bis(2-chloroisopropyl)ether,'' but use the correct CAS number of 108–60–1.

TABLE ID—LIST OF APPROVED TEST PROCEDURES FOR PESTICIDES [1]

Parameter	Method	EPA [2 7 10]	Standard methods	ASTM	Other
1. Aldrin	GC	617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96 (02).	See footnote,[3] p. 7; See footnote,[4] O–3104–83; See footnote, [8] 3M0222.
	GC/MS	625.1	6410 B–2000.		
2. Ametryn	GC	507, 619			See footnote,[3] p. 83; See footnote,[9] O–3106–93; See footnote,[6] p. S68.
	GC/MS	525.2, 625.1			See footnote,[14] O–1121–91.
3. Aminocarb	TLC				See footnote,[3] p. 94; See footnote,[6] p. S60.
	HPLC	632.			
4. Atraton	GC	619			See footnote,[3] p. 83; See footnote,[6] p. S68.
	GC/MS	625.1.			
5. Atrazine	GC	507, 619, 608.3			See footnote,[3] p. 83; See footnote,[6] p. S68; See footnote,[9] O–3106–93.
	HPLC/MS				See footnote,[12] O–2060–01.
	GC/MS	525.1, 525.2, 625.1			See footnote,[11] O–1126–95.
6. Azinphos methyl	GC	614, 622, 1657			See footnote,[3] p. 25; See footnote,[6] p. S51.
	GC–MS	625.1			See footnote,[11] O–1126–95.
7. Barban	TLC				See footnote,[3] p. 104; See footnote,[6] p. S64.
	HPLC	632.			
	GC/MS	625.1.			
8. α-BHC	GC	617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[8] 3M0222.
	GC/MS	625.1 [5]	6410 B–2000		See footnote,[11] O–1126–95.
9. β-BHC	GC	617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[8] 3M0222.
	GC/MS	625.1	6410 B–2000.		
10. δ-BHC	GC	617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[8] 3M0222.
	GC/MS	625.1	6410 B–2000.		
11. γ-BHC (Lindane)	GC	617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[4] O–3104–83; See footnote,[8] 3M0222.
	GC/MS	625.1 [5]	6410 B–2000		See footnote,[11] O–1126–95.
12. Captan	GC	617, 608.3	6630 B–2007	D3086–90, D5812–96(02).	See footnote,[3] p. 7.
13. Carbaryl	TLC				See footnote,[3] p. 94, See footnote,[6] p. S60.

TABLE ID—LIST OF APPROVED TEST PROCEDURES FOR PESTICIDES [1]—Continued

Parameter	Method	EPA [2 7 10]	Standard methods	ASTM	Other
	HPLC	531.1, 632.			
	HPLC/MS	553			See footnote,[12] O–2060–01.
	GC/MS	625.1			See footnote,[11] O–1126–95.
14. Carbophenothion	GC	617, 608.3	6630 B–2007		See footnote,[4] page 27; See footnote,[6] p. S73.
	GC/MS	625.1.			
15. Chlordane	GC	617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[4] O–3104–83; See footnote,[8] 3M0222.
	GC/MS	625.1	6410 B–2000.		
16. Chloropropham	TLC				See footnote,[3] p. 104; See footnote,[6] p. S64.
	HPLC	632.			
	GC/MS	625.1.			
17. 2,4-D	GC	615	6640 B–2006		See footnote,[3] p. 115; See footnote,[4] O–3105–83.
	HPLC/MS				See footnote,[12] O–2060–01.
18. 4,4′-DDD	GC	617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[4] O–3105–83; See footnote,[8] 3M0222.
	GC/MS	625.1	6410 B–2000.		
19. 4,4′-DDE	GC	617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[4] O–3104–83; See footnote,[8] 3M0222.
	GC/MS	625.1	6410 B–2000		See footnote,[11] O–1126–95.
20. 4,4′-DDT	GC	617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[4] O–3104–83; See footnote,[8] 3M0222.
	GC/MS	625.1	6410 B–2000.		
21. Demeton-O	GC	614, 622			See footnote,[3] p. 25; See footnote,[6] p. S51.
	GC/MS	625.1.			
22. Demeton-S	GC	614, 622			See footnote,[3] p. 25; See footnote,[6] p. S51.
	GC/MS	625.1.			
23. Diazinon	GC	507, 614, 622, 1657.			See footnote,[3] p. 25; See footnote,[4] O–3104–83; See footnote,[6] p. S51.
	GC/MS	525.2, 625.1			See footnote,[11] O–1126–95.
24. Dicamba	GC	615			See footnote,[3] p. 115.
	HPLC/MS				See footnote,[12] O–2060–01.
25. Dichlofenthion	GC	622.1			See footnote,[4] page 27; See footnote,[6] p. S73.
26. Dichloran	GC	608.2, 617, 608.3	6630 B–2007		See footnote,[3] p. 7;
27. Dicofol	GC	617, 608.3			See footnote,[4] O–3104–83.
28. Dieldrin	GC	617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[4] O–3104–83; See footnote,[8] 3M0222.
	GC/MS	625.1	6410 B–2000		See footnote,[11] O–1126–95.
29. Dioxathion	GC	614.1, 1657			See footnote,[4] page 27; See footnote,[6] p. S73.
30. Disulfoton	GC	507, 614, 622, 1657.			See footnote,[3] p. 25; See footnote,[6] p. S51.
	GC/MS	525.2, 625.1			See footnote,[11] O–1126–95.
31. Diuron	TLC				See footnote,[3] p. 104; See footnote,[6] p. S64.

TABLE ID—LIST OF APPROVED TEST PROCEDURES FOR PESTICIDES [1]—Continued

Parameter	Method	EPA [2 7 10]	Standard methods	ASTM	Other
	HPLC	632.			
	HPLC/MS	553			See footnote,[12] O–2060–01.
32. Endosulfan I	GC	617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[4] O–3104–83; See footnote,[8] 3M0222.
	GC/MS	625.1 [5]	6410 B–2000		See footnote,[13] O–2002–01.
33. Endosulfan II	GC	617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[8] 3M0222.
	GC/MS	625.1 [5]	6410 B–2000		See footnote,[13] O–2002–01.
34. Endosulfan Sulfate	GC	617, 608.3	6630 C–2007		See footnote,[8] 3M0222.
	GC/MS	625.1	6410 B–2000.		
35. Endrin	GC	505, 508, 617, 1656, 608.3.	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[4] O–3104–83; See footnote,[8] 3M0222.
	GC/MS	525.1, 525.2, 625.1 [5].	6410 B–2000.		
36. Endrin aldehyde	GC	617, 608.3	6630 C–2007		See footnote,[8] 3M0222.
	GC/MS	625.1.			
37. Ethion	GC	614, 614.1,1657			See footnote,[4] page 27; See footnote,[6] p. S73.
	GC/MS	625.1			See footnote,[13] O–2002–01.
38. Fenuron	TLC				See footnote,[3] p. 104; See footnote,[6] p. S64.
	HPLC	632.			
	HPLC/MS				See footnote,[12] O–2060–01.
39. Fenuron-TCA	TLC				See footnote,[3] p. 104; See footnote,[6] p. S64.
	HPLC	632.			
40. Heptachlor	GC	505, 508, 617, 1656, 608.3.	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[4] O–3104–83; See footnote,[8] 3M0222.
	GC/MS	525.1, 525.2, 625.1	6410 B–2000.		
41. Heptachlor epoxide	GC	617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[4] O–3104–83; See footnote,[6] p. S73; See footnote,[8] 3M0222.
	GC/MS	625.1	6410 B–2000.		
42. Isodrin	GC	617, 608.3	6630 B–2007 & C–2007.		See footnote,[4] O–3104–83; See footnote,[6] p. S73.
	GC/MS	625.1.			
43. Linuron	GC				See footnote,[3] p. 104; See footnote,[6] p. S64.
	HPLC	632.			
	HPLC/MS	553			See footnote,[12] O–2060–01.
	GC/MS				Seeootnote,[11] O–1126–95.
44. Malathion	GC	614, 1657	6630 B–2007		See footnote,[3] p. 25; See footnote,[6] p. S51.
	GC/MS	625.1			See footnote,[11] O–1126–95.
45. Methiocarb	TLC				See footnote,[3] p. 94; See footnote,[6] p. S60.
	HPLC	632.			
	HPLC/MS				See footnote,[12] O–2060–01.
46. Methoxychlor	GC	505, 508, 608.2, 617, 1656, 608.3.	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[4] O–3104–83; See footnote,[8] 3M0222.

TABLE ID—LIST OF APPROVED TEST PROCEDURES FOR PESTICIDES [1]—Continued

Parameter	Method	EPA [2 7 10]	Standard methods	ASTM	Other
	GC/MS	525.1, 525.2, 625.1			See footnote,[11] O–1126–95.
47. Mexacarbate	TLC				See footnote,[3] p. 94; See footnote,[6] p. S60.
	HPLC	632.			
	GC/MS	625.1.			
48. Mirex	GC	617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[4] O–3104–83.
	GC/MS	625.1.			
49. Monuron	TLC				See footnote,[3] p. 104; See footnote,[6] p. S64.
	HPLC	632.			
50. Monuron-TCA	TLC				See footnote,[3] p. 104; See footnote,[6] p. S64.
	HPLC	632.			
51. Neburon	TLC				See footnote,[3] p. 104; See footnote,[6] p. S64.
	HPLC	632.			
	HPLC/MS				See footnote,[12] O–2060–01.
52. Parathion methyl	GC	614, 622, 1657	6630 B–2007		See footnote,[4] page 27; See footnote,[3] p. 25.
	GC/MS	625.1			See footnote,[11] O–1126–95.
53. Parathion ethyl	GC	614	6630 B–2007		See footnote,[4] page 27; See footnote,[3] p. 25.
	GC/MS				See footnote,[11] O–1126–95.
54. PCNB	GC	608.1, 617, 608.3	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7.
55. Perthane	GC	617, 608.3		D3086–90, D5812–96(02).	See footnote,[4] O–3104–83.
56. Prometon	GC	507, 619			See footnote,[3] p. 83; See footnote,[6] p. S68; See footnote,[9] O–3106–93.
	GC/MS	525.2, 625.1			See footnote,[11] O–1126–95.
57. Prometryn	GC	507, 619			See footnote,[3] p. 83; See footnote,[6] p. S68; See footnote,[9] O–3106–93.
	GC/MS	525.1, 525.2, 625.1			See footnote,[13] O–2002–01.
58. Propazine	GC	507, 619, 1656, 608.3.			See footnote,[3] p. 83; See footnote,[6] p. S68; See footnote,[9] O–3106–93.
	GC/MS	525.1, 525.2, 625.1.			
59. Propham	TLC				See footnote,[3] p. 104; See footnote,[6] p. S64.
	HPLC	632.			
	HPLC/MS				See footnote,[12] O–2060–01.
60. Propoxur	TLC				See footnote,[3] p. 94; See footnote,[6] p. S60.
	HPLC	632.			
61. Secbumeton	TLC				See footnote,[3] p. 83; See footnote,[6] p. S68.
	GC	619.			
62. Siduron	TLC				See footnote,[3] p. 104; See footnote,[6] p. S64.
	HPLC	632.			
	HPLC/MS				See footnote,[12] O–2060–01.
63. Simazine	GC	505, 507, 619, 1656, 608.3.			See footnote,[3] p. 83; See footnote,[6] p. S68; See footnote,[9] O–3106–93.
	GC/MS	525.1, 525.2, 625.1			See footnote,[11] O–1126–95.
64. Strobane	GC	617, 608.3	6630 B–2007 & C–2007.		See footnote,[3] p. 7.
65. Swep	TLC				See footnote,[3] p. 104; See footnote,[6] p. S64.

TABLE ID—LIST OF APPROVED TEST PROCEDURES FOR PESTICIDES [1]—Continued

Parameter	Method	EPA [2 7 10]	Standard methods	ASTM	Other
	HPLC	632.			
66. 2,4,5-T	GC	615	6640 B–2006		See footnote,[3] p. 115; See footnote,[4] O–3105–83.
67. 2,4,5-TP (Silvex)	GC	615	6640 B–2006		See footnote,[3] p. 115; See footnote,[4] O–3105–83.
68. Terbuthylazine	GC	619, 1656, 608.3			See footnote,[3] p. 83; See footnote,[6] p. S68.
	GC/MS				See footnote,[13] O–2002–01.
69. Toxaphene	GC	505, 508, 617, 1656, 608.3.	6630 B–2007 & C–2007.	D3086–90, D5812–96(02).	See footnote,[3] p. 7; See footnote,[8]; See footnote,[4] O–3105–83.
	GC/MS	525.1, 525.2, 625.1	6410 B–2000.		
70. Trifluralin	GC	508, 617, 627, 1656, 608.3.	6630 B–2007		See footnote,[3] p. 7; See footnote,[9] O–3106–93.
	GC/MS	525.2, 625.1			See footnote,[11] O–1126–95.

Table ID notes:

[1] Pesticides are listed in this table by common name for the convenience of the reader. Additional pesticides may be found under Table IC, where entries are listed by chemical name.

[2] The standardized test procedure to be used to determine the method detection limit (MDL) for these test procedures is given at Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, of this Part 136.

[3] Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater. September 1978. U.S. EPA. This EPA publication includes thin-layer chromatography (TLC) methods.

[4] Methods for the Determination of Organic Substances in Water and Fluvial Sediments, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A3. 1987. USGS.

[5] The method may be extended to include α-BHC, γ-BHC, endosulfan I, endosulfan II, and endrin. However, when they are known to exist, Method 608.3 is the preferred method.

[6] Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency, Supplement to the 15th Edition of *Standard Methods for the Examination of Water and Wastewater.* 1981. American Public Health Association (APHA).

[7] Each analyst must make an initial, one-time, demonstration of their ability to generate acceptable precision and accuracy with Methods 608.3 and 625.1 in accordance with procedures given in Section 8.2 of each of these methods. Additionally, each laboratory, on an on-going basis, must spike and analyze 5% of all samples analyzed with Method 608.3 or 5% of all samples analyzed with Method 625.1 to monitor and evaluate laboratory data quality in accordance with Sections 8.3 and 8.4 of these methods. When the recovery of any parameter falls outside the warning limits, the analytical results for that parameter in the unspiked sample are suspect. The results should be reported, but cannot be used to demonstrate regulatory compliance. These quality control requirements also apply to the Standard Methods, ASTM Methods, and other methods cited.

[8] Organochlorine Pesticides and PCBs in Wastewater Using Empore™ Disk. Revised October 28, 1994. 3M Corporation.

[9] Method O–3106–93 is in Open File Report 94–37, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Triazine and Other Nitrogen-Containing Compounds by Gas Chromatography With Nitrogen Phosphorus Detectors. 1994. USGS.

[10] EPA Methods 608.1, 608.2, 614, 614.1, 615, 617, 619, 622, 622.1, 627, and 632 are found in Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, EPA 821–R–92–002, April 1992, U.S. EPA. EPA Methods 505, 507, 508, 525.1, 531.1 and 553 are in Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, Volume II, EPA 821–R–93–010B, 1993, U.S. EPA. EPA Method 525.2 is in Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry, Revision 2.0, 1995, U.S. EPA. EPA methods 1656 and 1657 are in Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, Volume I, EPA 821–R–93–010A, 1993, U.S. EPA. Methods 608.3 and 625.1 are available at: *http://water.epa.gov/scitech/methods/cwa/methods_index.cfm* (this is a placeholder for now).

[11] Method O–1126–95 is in Open-File Report 95–181, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by C–18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring. 1995. USGS.

[12] Method O–2060–01 is in Water-Resources Investigations Report 01–4134, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Pesticides in Water by Graphitized Carbon-Based Solid-Phase Extraction and High-Performance Liquid Chromatography/Mass Spectrometry. 2001. USGS.

[13] Method O–2002–01 is in Water-Resources Investigations Report 01–4098, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of moderate-use pesticides in water by C–18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry. 2001. USGS.

[14] Method O–1121–91 is in Open-File Report 91–519, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of organonitrogen herbicides in water by solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring. 1992. USGS.

* * * * *

TABLE 1F—LIST OF APPROVED METHODS FOR PHARMACEUTICAL POLLUTANTS

Pharmaceuticals pollutants	CAS Registry No.	Analytical method number
Acetonitrile	75–05–8	1666/1671/D3371/D3695/624.1.
n-Amyl acetate	628–63–7	1666/D3695.
n-Amyl alcohol	71–41–0	1666/D3695.
Benzene	71–43–2	D4763/D3695/502.2/524.2/624.1.

TABLE 1F—LIST OF APPROVED METHODS FOR PHARMACEUTICAL POLLUTANTS—Continued

Pharmaceuticals pollutants	CAS Registry No.	Analytical method number
n-Butyl-acetate	123–86–4	1666/D3695.
tert-Butyl alcohol	75–65–0	1666/624.1.
Chlorobenzene	108–90–7	502.2/524.2/624.1.
Chloroform	67–66–3	502.2/524.2/551/624.1.
o-Dichlorobenzene	95–50–1	1625C/502.2/524.2/624.1.
1,2-Dichloroethane	107–06–2	D3695/502.2/524.2/624.1.
Diethylamine	109–89–7	1666/1671.
Dimethyl sulfoxide	67–68–5	1666/1671.
Ethanol	64–17–5	1666/1671/D3695/624.1.
Ethyl acetate	141–78–6	1666/D3695/624.1.
n-Heptane	142–82–5	1666/D3695.
n-Hexane	110–54–3	1666/D3695.
Isobutyraldehyde	78–84–2	1666/1667.
Isopropanol	67–63–0	1666/D3695.
Isopropyl acetate	108–21–4	1666/D3695.
Isopropyl ether	108–20–3	1666/D3695.
Methanol	67–56–1	1666/1671/D3695/624.1.
Methyl Cellosolve ® (2-Methoxy ethanol)	109–86–4	1666/1671.
Methylene chloride	75–09–2	502.2/524.2/624.1.
Methyl formate	107–31–3	1666.
4-Methyl-2-pentanone (MIBK)	108–10–1	1624C/1666/D3695/D4763/524.2/624.1.
Phenol	108–95–2	D4763.
n-Propanol	71–23–8	1666/1671/D3695/624.1.
2-Propanone (Acetone)	67–64–1	D3695/D4763/524.2/624.1.
Tetrahydrofuran	109–99–9	1666/524.2/624.1.
Toluene	108–88–3	D3695/D4763/502.2/524.2/624.1.
Triethlyamine	121–44–8	1666/1671.
Xylenes	(Note 1)	1624C/1666/624.1.

Table 1F note:
[1] 1624C: *m*-xylene 108–38–3, *o,p*-xylene, E–14095 (Not a CAS number; this is the number provided in the Environmental Monitoring Methods Index [EMMI] database.); 1666: m,p-xylene 136777–61–2, *o*-xylene 95–47–6.

TABLE 1G—TEST METHODS FOR PESTICIDE ACTIVE INGREDIENTS (40 CFR PART 455)

EPA survey code	Pesticide name	CAS No.	EPA analytical method No.(s) [3]
8	Triadimefon	43121–43–3	507/633/525.1/525.2/1656/625.1.
12	Dichlorvos	62–73–7	1657/507/622/525.1/525.2/625.1.
16	2,4–D; 2,4–D Salts and Esters [2,4-Dichlorophenoxyacetic acid].	94–75–7	1658/515.1/615/515.2/555.
17	2,4–DB; 2,4–DB Salts and Esters [2,4-Dichlorophenoxybutyric acid].	94–82–6	1658/515.1/615/515.2/555.
22	Mevinphos	7786–34–7	1657/507/622/525.1/525.2/625.1.
25	Cyanazine	21725–46–2	629/507/608.3/625.1.
26	Propachlor	1918–16–7	1656/508/608.1/525.1/525.2/608.3/625.1.
27	MCPA; MCPA Salts and Esters [2-Methyl-4-chlorophenoxyacetic acid].	94–74–6	1658/615/555.
30	Dichlorprop; Dichlorprop Salts and Esters [2-(2,4-Dichlorophenoxy) propionic acid].	120–36–5	1658/515.1/615/515.2/555.
31	MCPP; MCPP Salts and Esters [2-(2-Methyl-4-chlorophenoxy) propionic acid].	93–65–2	1658/615/555.
35	TCMTB [2-(Thiocyanomethylthio) benzo-thiazole].	21564–17–0	637.
39	Pronamide	23950–58–5	525.1/525.2/507/633.1/625.1.
41	Propanil	709–98–8	632.1/1656/608.3.
45	Metribuzin	21087–64–9	507/633/525.1/525.2/1656/608.3/6 625.1.
52	Acephate	30560–19–1	1656/1657/608.3.
53	Acifluorfen	50594–66–6	515.1/515.2/555.
54	Alachlor	15972–60–8	505/507/645/525.1/525.2/1656/608.3/625.1.
55	Aldicarb	116–06–3	531.1.
58	Ametryn	834–12–8	507/619/525.2/625.1.
60	Atrazine	1912–24–9	505/507/619/525.1/525.2/1656/6 608.3/625.1.
62	Benomyl	17804–35–2	631.
68	Bromacil; Bromacil Salts and Esters	314–40–9	507/633/525.1/525.2/1656/608.3/6 625.1.
69	Bromoxynil	1689–84–5	1625/1661/625.1.
69	Bromoxynil octanoate	1689–99–2	1656/608.3.
70	Butachlor	23184–66–9	507/645/525.1/525.2/1656/608.3/625.1.
73	Captafol	2425–06–1	1656/608.3/625.1.
75	Carbaryl [Sevin]	63–25–2	531.1/632/553/625.1.
76	Carbofuran	1563–66–2	531.1/632/625.1.

TABLE 1G—TEST METHODS FOR PESTICIDE ACTIVE INGREDIENTS (40 CFR PART 455)—Continued

EPA survey code	Pesticide name	CAS No.	EPA analytical method No.(s) [3]
80	Chloroneb	2675–77–6	1656/508/608.1/525.1/525.2/608.3/625.1.
82	Chlorothalonil	1897–45–6	508/608.2/525.1/525.2/1656/608.3/625.1.
84	Stirofos	961–11–5	1657/507/622/525.1/525.2/625.1.
86	Chlorpyrifos	2921–88–2	1657/508/622/625.1.
90	Fenvalerate	51630–58–1	1660.
103	Diazinon	333–41–5	1657/507/614/622/525.2/625.1.
107	Parathion methyl	298–00–0	1657/614/622/625.1.
110	DCPA [Dimethyl 2,3,5,6-tetrachloroterephthalate].	1861–32–1	508/608.2/525.1/525.2/515.1 [2]/515.2 [2]/1656/608.3/625.1.
112	Dinoseb	88–85–7	1658/515.1/615/515.2/555/625.1.
113	Dioxathion	78–34–2	1657/614.1.
118	Nabonate [Disodium cyanodithioimidocarbonate].	138–93–2	630.1.
119	Diuron	330–54–1	632/553.
123	Endothall	145–73–3	548/548.1.
124	Endrin	72–20–8	1656/505/508/617/525.1/525.2/608.3/625.1.
125	Ethalfluralin	55283–68–6	1656/627/608.3 See footnote 1.
126	Ethion	563–12–2	1657/614/614.1/625.1.
127	Ethoprop	13194–48–4	1657/507/622/525.1/525.2/625.1.
132	Fenarimol	60168–88–9	507/633.1/525.1/525.2/1656/608.3/625.1.
133	Fenthion	55–38–9	1657/622/625.1.
138	Glyphosate [N-(Phosphonomethyl) glycine]	1071–83–6	547.
140	Heptachlor	76–44–8	1656/505/508/617/525.1/525.2/608.3/625.1.
144	Isopropalin	33820–53–0	1656/627/608.3.
148	Linuron	330–55–2	553/632.
150	Malathion	121–75–5	1657/614/625.1.
154	Methamidophos	10265–92–6	1657.
156	Methomyl	16752–77–5	531.1/632.
158	Methoxychlor	72–43–5	1656/505/508/608.2/617/525.1/525.2/608.3/625.1.
172	Nabam	142–59–6	630/630.1.
173	Naled	300–76–5	1657/622/625.1.
175	Norflurazon	27314–13–2	507/645/525.1/525.2/1656/608.3/625.1.
178	Benfluralin	1861–40–1	1656/627/608.3 See footnote 1.
182	Fensulfothion	115–90–2	1657/622/625.1.
183	Disulfoton	298–04–4	1657/507/614/622/525.2/625.1.
185	Phosmet	732–11–6	1657/622.1/625.1.
186	Azinphos Methyl	86–50–0	1657/614/622/625.1.
192	Organo-tin pesticides	12379–54–3	Ind-01/200.7/200.9.
197	Bolstar	35400–43–2	1657/622.
203	Parathion	56–38–2	1657/614/625.1.
204	Pendimethalin	40487–42–1	1656.
205	Pentachloronitrobenzene	82–68–8	1656/608.1/617/608.3/625.1.
206	Pentachlorophenol	87–86–5	1625/515.2/555/515.1/525.1/525.2/625.1.
208	Permethrin	52645–53–1	608.2/508/525.1/525.2/1656/1660/608.3 [4]/625.1 [4].
212	Phorate	298–02–2	1657/622/625.1.
218	Busan 85 [Potassium dimethyldithiocarbamate].	128–03–0	630/630.1.
219	Busan 40 [Potassium N-hydroxymethyl-N-methyldithiocarbamate].	51026–28–9	630/630.1.
220	KN Methyl [Potassium N-methyldithiocarbamate].	137–41–7	630/630.1.
223	Prometon	1610–18–0	507/619/525.2/625.1.
224	Prometryn	7287–19–6	507/619/525.1/525.2/625.1.
226	Propazine	139–40–2	507/619/525.1/525.2/1656/608.3/625.1.
230	Pyrethrin I	121–21–1	1660.
232	Pyrethrin II	121–29–9	1660.
236	DEF [S,S,S-Tributyl phosphorotrithioate]	78–48–8	1657.
239	Simazine	122–34–9	505/507/619/525.1/525.2/1656/608.3/625.1.
241	Carbam-S [Sodium dimethyldithio-carbamate]	128–04–1	630/630.1.
243	Vapam [Sodium methyldithiocarbamate]	137–42–8	630/630.1.
252	Tebuthiuron	34014–18–1	507/525.1/525.2/625.1.
254	Terbacil	5902–51–2	507/633/525.1/525.2/1656/608.3/625.1.
255	Terbufos	13071–79–9	1657/507/614.1/525.1/525.2/625.1.
256	Terbuthylazine	5915–41–3	619/1656/608.3.
257	Terbutryn	886–50–0	507/619/525.1/525.2/625.1.
259	Dazomet	533–74–4	630/630.1/1659.
262	Toxaphene	8001–35–2	1656/505/508/617/525.1/525.2/608.3/625.1.
263	Merphos [Tributyl phosphorotrithioate]	150–50–5	1657/507/525.1/525.2/622/625.1.
264	Trifluralin [1]	1582–09–8	1656/508/617/627/525.2/608.3/625.1.

TABLE 1G—TEST METHODS FOR PESTICIDE ACTIVE INGREDIENTS (40 CFR PART 455)—Continued

EPA survey code	Pesticide name	CAS No.	EPA analytical method No.(s) [3]
268	Ziram [Zinc dimethyldithiocarbamate]	137–30–4	630/630.1.

Table 1G notes:

[1] Monitor and report as total Trifluralin.

[2] Applicable to the analysis of DCPA degradates.

[3] EPA Methods 608.1 through 645, 1645 through 1661, and Ind-01 are available in Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, Volume I, EPA 821–R–93–010A, Revision I, August 1993, U.S. EPA. EPA Methods 200.9 and 505 through 555 are available in Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, Volume II, EPA 821–R–93–010B, August 1993, U.S. EPA. The full text of Methods 608.3, 625.1, and 1625 are provided at Appendix A of this part 136. The full text of Method 200.7 is provided at Appendix C of this part 136. Methods 608.3 and 625.1 are available at: *http://water.epa.gov/scitech/methods/cwa/methods_index.cfm* (this is a placeholder for now).

[4] Permethrin is not listed within methods 608.3 and 625.1; however, cis-permethrin and trans-permethrin are listed. Permethrin can be calculated by adding the results of cis and trans-permethrin.

TABLE 1H—LIST OF APPROVED MICROBIOLOGICAL METHODS FOR AMBIENT WATER

Parameter and units	Method [1]	EPA	Standard methods	AOAC, ASTM, USGS	Other
Bacteria:					
1. Coliform (fecal), number per 100 mL or number per gram dry weight.	Most Probable Number (MPN), 5 tube, 3 dilution, or.	p. 132 [3]	9221 C E–2006		
	Membrane filter (MF),[2] single step.	p. 124 [3]	9222 D–2006 [27]	B–0050–85 [4]	
2. Coliform (fecal) in presence of chlorine, number per 100 mL.	MPN, 5 tube, 3 dilution, or	p. 132 [3]	9221 C E–2006		
	MF [2], single step [5]	p. 124 [3]	9222 D–2006 [27]		
3. Coliform (total), number per 100 mL	MPN, 5 tube, 3 dilution, or	p. 114 [3]	9221 B–2006		
	MF [2], single step or two step	p. 108 [3]	9222 B–2006	B–0025–85 [4]	
4. Coliform (total), in presence of chlorine, number per 100 mL.	MPN, 5 tube, 3 dilution, or	p. 114 [3]	9221 B–2006		
	MF [2] with enrichment	p. 111 [3]	9222 B–2006		
5. *E. coli,* number per 100 mL	MPN,[6 8 14] multiple tube, or		9221 B.2–2006/9221 F–2006 [11 13]		
	Multiple tube/multiple well, or		9223 B–2004 [12]	991.15 [10]	Colilert® [12 16], Colilert-® [12 15 16]
	MF [2 5 6 7 8], two step, or	1103.1 [19]	9222 B–2006/9222 G–2006,[18] 9213 D–2007	D5392–93 [9]	
	Single step	1603 [20], 1604 [21].			mColiBlue–24® [17]
6. Fecal streptococci, number per 100 mL	MPN, 5 tube, 3 dilution, or	p. 139 [3]	9230 B–2007		
	MF [2], or	p. 136 [3]	9230 C–2007	B–0055–85 [4]	
	Plate count	p. 143 [3].			
7. Enterococci, number per 100 mL	MPN,[6 8] multiple tube/multiple well, or.		9230 D–2007	D6503–99 [9]	Enterolert® [12 22]
	MF [2 5 6 7 8] two step, or	1106.1 [23]	9230 C–2007	D5259–92 [9]	
	Single step, or	1600 [24]	9230 C–2007		
	Plate count	p. 143 [3].			
Protozoa:.					
8. *Cryptosporidium*	Filtration/IMS/FA	1622 [25], 1623 [26].			
9. *Giardia*	Filtration/IMS/FA	1623 [26].			

Table 1H notes:

[1] The method must be specified when results are reported.

[2] A 0.45-µm membrane filter (MF) or other pore size certified by the manufacturer to fully retain organisms to be cultivated and to be free of extractables which could interfere with their growth.

[3] Microbiological Methods for Monitoring the Environment, Water, and Wastes. EPA/600/8–78/017. 1978. US EPA.

[4] U.S. Geological Survey Techniques of Water-Resource Investigations, Book 5, Laboratory Analysis, Chapter A4, Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples. 1989. USGS.

[5] Because the MF technique usually yields low and variable recovery from chlorinated wastewaters, the Most Probable Number method will be required to resolve any controversies.

[6] Tests must be conducted to provide organism enumeration (density). Select the appropriate configuration of tubes/filtrations and dilutions/volumes to account for the quality, character, consistency, and anticipated organism density of the water sample.

[7] When the MF method has not been used previously to test waters with high turbidity, large numbers of noncoliform bacteria, or samples that may contain organisms stressed by chlorine, a parallel test should be conducted with a multiple-tube technique to demonstrate applicability and comparability of results.

[8] To assess the comparability of results obtained with individual methods, it is suggested that side-by-side tests be conducted across seasons of the year with the water samples routinely tested in accordance with the most current Standard Methods for the Examination of Water and Wastewater or EPA alternate test procedure (ATP) guidelines.

[9] Annual Book of ASTM Standards—Water and Environmental Technology. Section 11.02. 2000, 1999, 1996. ASTM International.

[10] Official Methods of Analysis of AOAC International, 16th Edition, Volume I, Chapter 17. 1995. AOAC International.

[11] The multiple-tube fermentation test is used in 9221B.2–2006. Lactose broth may be used in lieu of lauryl tryptose broth (LTB), if at least 25 parallel tests are conducted between this broth and LTB using the water samples normally tested, and this comparison demonstrates that the false-positive rate and false-negative rate for total coliform using lactose broth is less than 10 percent. No requirement exists to run the completed phase on 10 percent of all total coliform-positive tubes on a seasonal basis.

[12] These tests are collectively known as defined enzyme substrate tests, where, for example, a substrate is used to detect the enzyme β-glucuronidase produced by *E. coli.*

[13] After prior enrichment in a presumptive medium for total coliform using 9221B.2–2006, all presumptive tubes or bottles showing any amount of gas, growth or acidity within 48 h ± 3 h of incubation shall be submitted to 9221F–2006. Commercially available EC–MUG media or EC media supplemented in the laboratory with 50 μg/mL of MUG may be used.

[14] Samples shall be enumerated by the multiple-tube or multiple-well procedure. Using multiple-tube procedures, employ an appropriate tube and dilution configuration of the sample as needed and report the Most Probable Number (MPN). Samples tested with Colilert® may be enumerated with the multiple-well procedures, Quanti-Tray® or Quanti-Tray®/2000, and the MPN calculated from the table provided by the manufacturer.

[15] Colilert-18® is an optimized formulation of the Colilert® for the determination of total coliforms and *E. coli* that provides results within 18 h of incubation at 35 °C, rather than the 24 h required for the Colilert® test, and is recommended for marine water samples.

[16] Descriptions of the Colilert®, Colilert-18®, Quanti-Tray®, and Quanti-Tray®/2000 may be obtained from IDEXX Laboratories Inc.

[17] A description of the mColiBlue24® test may be obtained from Hach Company.

[18] Subject total coliform positive samples determined by 9222B–1997 or other membrane filter procedure to 9222G–1997 using NA–MUG media.

[19] Method 1103.1: *Escherichia coli* (*E. coli*) in Water by Membrane Filtration Using membrane-Thermotolerant *Escherichia coli* Agar (mTEC), EPA–821–R–10–002. March 2010. US EPA.

[20] Method 1603: *Escherichia coli* (*E. coli*) in Water by Membrane Filtration Using Modified membrane-Thermotolerant *Escherichia coli* Agar (Modified mTEC), EPA–821–R–14–010. September 2014. US EPA.

[21] Preparation and use of MI agar with a standard membrane filter procedure is set forth in the article, Brenner et al. 1993. New Medium for the Simultaneous Detection of Total Coliform and *Escherichia coli* in Water. Appl. Environ. Microbiol. 59:3534–3544 and in Method 1604: Total Coliforms and *Escherichia coli* (*E. coli*) in Water by Membrane Filtration by Using a Simultaneous Detection Technique (MI Medium), EPA 821–R–02–024, September 2002, US EPA.

[22] A description of the Enterolert® test may be obtained from IDEXX Laboratories Inc.

[23] Method 1106.1: Enterococci in Water by Membrane Filtration Using membrane-Enterococcus-Esculin Iron Agar (mE–EIA), EPA–821–R–09–015. December 2009. US EPA.

[24] Method 1600: Enterococci in Water by Membrane Filtration Using membrane-Enterococcus Indoxyl-β-D-Glucoside Agar (mEI), EPA–821–R–14–011. September 2014. US EPA.

[25] Method 1622 uses a filtration, concentration, immunomagnetic separation of oocysts from captured material, immunofluorescence assay to determine concentrations, and confirmation through vital dye staining and differential interference contrast microscopy for the detection of *Cryptosporidium.* Method 1622: *Cryptosporidium* in Water by Filtration/IMS/FA, EPA–821–R–05–001. December 2005. US EPA.

[26] Method 1623 uses a filtration, concentration, immunomagnetic separation of oocysts and cysts from captured material, immunofluorescence assay to determine concentrations, and confirmation through vital dye staining and differential interference contrast microscopy for the simultaneous detection of *Cryptosporidium* and *Giardia* oocysts and cysts. Method 1623: *Cryptosporidium* and *Giardia* in Water by Filtration/IMS/FA. EPA–821–R–05–002. December 2005. US EPA.

[27] The verification frequency is at least five typical and five atypical colonies per sampling site on the day of sample collection and analysis.

(b) The documents required in this section are incorporated by reference into this section in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies of the documents may be obtained from the sources listed in paragraph (b) of this section. Documents may be inspected at EPA's Water Docket, EPA West, 1301 Constitution Avenue NW., Room 3334, Washington, DC 20004, (Telephone: 202–566–2426); or at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202–741–6030, or go to: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html.* These test procedures are incorporated as they exist on the day of approval and a notice of any change in these test procedures will be published in the **Federal Register**. The full texts of the methods from the following references which are cited in Tables IA, IB, IC, ID, IE, IF, IG and IH of this section are incorporated by reference into this regulation and may be obtained from the source identified.

* * * * *

(8) * * *

* * * * *

(iv) Method 1600: Enterococci in Water by Membrane Filtration Using membrane-Enterococcus Indoxyl-β-D-Glucoside Agar (mEI). September 2014. EPA–821–R–14–011. Table IA, Note 25; Table IH, Note 24.

(v) Method 1603: *Escherichia coli* (*E. coli*) in Water by Membrane Filtration Using Modified membrane-Thermotolerant *Escherichia coli* Agar (Modified mTEC). September 2014. EPA–821–R–14–010. Table IA, Note 22; Table IH, Note 20.

* * * * *

(xiii) Method 1680: Fecal Coliforms in Sewage Sludge (Biosolids) by Multiple-Tube Fermentation using Lauryl Tryptose Broth (LTB) and EC Medium. September 2014. EPA–821–R–14–009. Table IA, Note 15.

* * * * *

(xv) Method 1682: *Salmonella* in Sewage Sludge (Biosolids) by Modified Semisolid Rappaport-Vassiliadis (MSRV) Medium. September 2014. EPA 821–R–14–012. Table IA, Note 23.

* * * * *

(10) * * *

* * * * *

(viii) 2120, Color. 2011. Table IB.

* * * * *

(x) 2310, Acidity. 2011. Table IB.

(xi) 2320, Alkalinity. 2011. Table IB.

(xii) 2340, Hardness. 2011. Table IB.

(xiii) 2510, Conductivity. 2011. Table IB.

(xiv) 2540, Solids. 2011. Table IB.

(xv) 2550, Temperature. 2011. Table IB.

(xvi) 3111, Metals by Flame Atomic Absorption Spectrometry. 2011. Table IB.

(xvii) 3112, Metals by Cold-Vapor Atomic Absorption Spectrometry. 2011. Table IB.

(xviii) 3113, Metals by Electrothermal Atomic Absorption Spectrometry. 2010. Table IB.

(xix) 3114, Arsenic and Selenium by Hydride Generation/Atomic Absorption Spectrometry. 2011. Table IB.

(xx) 3120, Metals by Plasma Emission Spectroscopy. 2011. Table IB.

(xxi) 3125, Metals by Inductively Coupled Plasma-Mass Spectrometry. 2011. Table IB.

(xxii) 3500-Al, Aluminum. 2011. Table IB.

(xxiii) 3500-As, Arsenic. 2011. Table IB.

(xxiv) 3500-Ca, Calcium. 2011. Table IB.

(xxv) 3500-Cr, Chromium. 2011. Table IB.

(xxvi) 3500-Cu, Copper. 2011. Table IB.

(xxvii) 3500-Fe, Iron. 2011. Table IB.

(xxviii) 3500-Pb, Lead. 2011. Table IB.

(xxix) 3500-Mn, Manganese. 2011. Table IB.

(xxx) 3500-K, Potassium. 2011. Table IB.

(xxxi) 3500-Na, Sodium. 2011. Table IB.

(xxxii) 3500-V, Vanadium. 2011. Table IB.

(xxxiii) 3500-Zn, Zinc. 2011. Table IB.

(xxxiv) 4110, Determination of Anions by Ion Chromatography. 2011. Table IB.

(xxxv) 4140, Inorganic Anions by Capillary Ion Electrophoresis. 2011. Table IB.

(xxxvi) 4500-B, Boron. 2011. Table IB.

(xxxvii) 4500-Cl^-, Chloride. 2011. Table IB.

(xxxviii) 4500-Cl, Chlorine (Residual). 2011. Table IB.

(xxxix) 4500-CN^-, Cyanide. 2011. Table IB.

(xl) 4500-F^-, Fluoride. 2011. Table IB.

(xli) 4500-H^+, pH Value. 2011. Table IB.

(xlii) 4500-NH_3, Nitrogen (Ammonia). 2011. Table IB.

(xliii) 4500-NO_2^-, Nitrogen (Nitrite). 2011. Table IB.

(xliv) 4500-NO_3^-, Nitrogen (Nitrate). 2011. Table IB.

(xlv) 4500-N_{org}, Nitrogen (Organic). 2011. Table IB.

(xlvi) 4500-O, Oxygen (Dissolved). 2011. Table IB.

(xlvii) 4500-P, Phosphorus. 2011. Table IB.

(xlviii) 4500-SiO_2, Silica. 2011. Table IB.

(xlix) 4500-$S^{2\cdot}$, Sulfide. 2011. Table IB.

(l) 4500-$SO_3^{2\cdot}$, Sulfite. 2011. Table IB.

(li) 4500-$SO_4^{2\cdot}$, Sulfate. 2011. Table IB.

(lii) 5210, Biochemical Oxygen Demand (BOD). 2011. Table IB.

(liii) 5220, Chemical Oxygen Demand (COD). 2011. Table IB.

(liv) 5310, Total Organic Carbon (TOC). 2011. Table IB.

(lv) 5520, Oil and Grease. 2011. Table IB.

(lvi) 5530, Phenols. 2010. Table IB.

(lvii) 5540, Surfactants. 2011. Table IB.

(lviii) 6200, Volatile Organic Compounds. 2011. Table IC.

* * * * *

(lxi) 6440, Polynuclear Aromatic Hydrocarbons. 2005. Table IC.

(lxii) 6630, Organochlorine Pesticides. 2007. Table ID.

(lxiii) 6640, Acidic Herbicide Compounds. 2006. Table ID.

* * * * *

(lxviii) 9222, Membrane Filter Technique for Members of the Coliform Group. 2006. Table IA; Table IH, Note 18.

* * * * *

(15) * * *

* * * * *

(v) ASTM D511–09, Standard Test Methods for Calcium and Magnesium in Water. May 2009. Table IB.

* * * * *

(viii) ASTM D516–11, Standard Test Method for Sulfate Ion in Water, September 2011. Table IB.

(ix) ASTM D858–12, Standard Test Methods for Manganese in Water. September 2012. Table IB.

(x) ASTM D859–10, Standard Test Method for Silica in Water. July 2010. Table IB.

* * * * *

(xii) ASTM D1067–11, Standard Test Methods for Acidity or Alkalinity of Water. April 2011. Table IB.

(xiii) ASTM D1068–10, Standard Test Methods for Iron in Water. October 2010. Table IB.

* * * * *

(xv) ASTM D1126–12, Standard Test Method for Hardness in Water. March 2012. Table IB.

(xvi) ASTM D1179–10, Standard Test Methods for Fluoride Ion in Water. July 2010. Table IB.

(xvii) ASTM D1246–10, Standard Test Method for Bromide Ion in Water. July 2010. Table IB.

* * * * *

(xxii) ASTM D1687–12 (Approved September 1, 2012), Standard Test Methods for Chromium in Water. August 2007. Table IB.

(xxiii) ASTM D1688–12, Standard Test Methods for Copper in Water. September 2012. Table IB.

(xxiv) ASTM D1691–12, Standard Test Methods for Zinc in Water. September 2012. Table IB.

* * * * *

(xxx) ASTM D1976–12, Standard Test Method for Elements in Water by Inductively-Coupled Argon Plasma Atomic Emission Spectroscopy. March 2012. Table IB.

* * * * *

(xxxv) ASTM D3223–12, Standard Test Method for Total Mercury in Water. September 2012. Table IB.

* * * * *

(xxxvii) ASTM D3373–12, Standard Test Method for Vanadium in Water. September 2012. Table IB.

* * * * *

(xxxix) ASTM D3557–12, Standard Test Method for Cadmium in Water. September 2012. Table IB.

* * * * *

(xlii) ASTM D3590–11, Standard Test Methods for Total Kjeldahl Nitrogen in Water. April 2011. Table IB.

* * * * *

(l) ASTM D4382–12, Standard Test Method for Barium in Water, Atomic Absorption Spectrophotometry, Graphite Furnace. September 2012. Table IB.

* * * * *

(lii) ASTM D4658–09, Standard Test Method for Sulfide Ion in Water. May 2009. Table IB.

* * * * *

(lv) ASTM D5257–11, Standard Test Method for Dissolved Hexavalent Chromium in Water by Ion Chromatography. April 2011. Table IB.

* * * * *

(lviii) ASTM D5673–10, Standard Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry. September 2010. Table IB.

(lix) ASTM D5907–13, Standard Test Method for Filterable and Nonfilterable Matter in Water. July 2013. Table IB.

* * * * *

(lxi) ASTM. D6508–10, Standard Test Method for Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis and Chromate Electrolyte. October 2010. Table IB, Note 54.

* * * * *

(lxvi) ASTM. D7284–13, Standard Test Method for Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection. July 2013. Table IB.

* * * * *

(lxviii) ASTM. D7511–12, Standard Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection. January 2012. Table IB.

* * * * *

(19) * * *

* * * * *

(vii) Method 10206, TNTplus 835–836 Nitrate Method, Spectrophotometric Measurement of Nitrate in Water and

Wastewater. Revision 2.1, January 10, 2013. Table IB, Note 75.

(viii) Method 10242, TNTplus 880 Total Kjeldahl Nitrogen Method, Simplified Spectrophotometric Measurement of Total Kjeldahl Nitrogen in Water and Wastewater. Revision 1.1, January 10, 2013. Table IB, Note 75.

* * * * *

(20) * * *

(i) Colilert®. 2013. Table IA, Notes 17 and 18; Table IH, Notes 14, 15 and 16.

(ii) Colilert-18®. 2013. Table IA, Notes 17 and 18; Table IH, Notes 14, 15 and 16.

(iii) Enterolert®. 2013. Table IA, Note 24; Table IH, Note 12.

(iv) Quanti-Tray®. 2013. Table IA, Note 18; Table IH, Notes 14 and 16.

* * * * *

(25) National Council of the Paper Industry for Air and Stream Improvements, Inc. (NCASI), 260 Madison Avenue, New York NY 10016.

(i) NCASI Methods TNTP–W10900 as an Alternative Testing Procedure to EPA Method 351.2 and EPA Method 365.4. June 2011. Table IB, Note 77.

(ii) NCASI Technical Bulletin No. 253, An Investigation of Improved Procedures for Measurement of Mill Effluent and Receiving Water Color. December 1971. Table IB, Note 18.

(iii) NCASI Technical Bulletin No. 803, An Update of Procedures for the Measurement of Color in Pulp Mill Wastewaters. May 2000. Table IB, Note 18.

(26) The Nitrate Elimination Co., Inc. (NECi), 334 Hecla St., Lake Linden NI 49945.

(i) NECi Method N07–0003, Method for Nitrate Reductase Nitrate-Nitrogen Analysis. Revision 9.0. March 2014. Table IB, Note 73.

(ii) [Reserved]

* * * * *

(34) Timberline Instruments, LLC, 1880 South Flatiron Ct., Unit I, Boulder CO 80301.

(i) Determination of Inorganic Ammonia by Continuous Flow Gas Diffusion and Conductivity Cell Analysis. June 24, 2011. Table IB, Note 74.

(ii) [Reserved]

(35) U.S. Geological Survey (USGS), U.S. Department of the Interior, Reston, Virginia. Available from USGS Books and Open-File Reports (OFR) Section, Federal Center, Box 25425, Denver, CO 80225.

(i) Colorimetric determination of nitrate plus nitrite in water by enzymatic reduction, automated discrete analyzer methods. U.S. Geological Survey Techniques and Methods, Book 5, Chapter B8. 2011. Table IB, Note 72.

(ii) Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, editors, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A1. 1979. Table IB, Note 8.

(iii) Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A1. 1989. Table IB, Note 2.

(iv) Methods for the Determination of Organic Substances in Water and Fluvial Sediments. Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A3. 1987. Table IB, Note 24; Table ID, Note 4.

(v) OFR 76–177, Selected Methods of the U.S. Geological Survey of Analysis of Wastewaters. 1976. Table IE, Note 2.

(vi) OFR 91–519, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Organonitrogen Herbicides in Water by Solid-Phase Extraction and Capillary-Column Gas Chromatography/Mass Spectrometry With Selected-Ion Monitoring. 1992. Table ID, Note 14.

(vii) OFR 92–146, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Total Phosphorus by a Kjeldahl Digestion Method and an Automated Colorimetric Finish That Includes Dialysis. 1992. Table IB, Note 48.

(viii) OFR 93–125, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments. 1993. Table IB, Note 51; Table IC, Note 9.

(ix) OFR 93–449, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Chromium in Water by Graphite Furnace Atomic Absorption Spectrophotometry. 1993. Table IB, Note 46.

(x) OFR 94–37, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Triazine and Other Nitrogen-containing Compounds by Gas Chromatography with Nitrogen Phosphorus Detectors. 1994. Table ID, Note 9.

(xi) OFR 95–181, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Pesticides in Water by C–18 Solid-Phase Extraction and Capillary-Column Gas Chromatography/Mass Spectrometry With Selected-Ion Monitoring. 1995. Table ID, Note 11.

(xii) OFR 97–198, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Molybdenum in Water by Graphite Furnace Atomic Absorption Spectrophotometry. 1997. Table IB, Note 47.

(xiii) OFR 98–165, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Elements in Whole-Water Digests Using Inductively Coupled Plasma-Optical Emission Spectrometry and Inductively Coupled Plasma-Mass Spectrometry. 1998. Table IB, Note 50.

(xiv) OFR 98–639, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Arsenic and Selenium in Water and Sediment by Graphite Furnace—Atomic Absorption Spectrometry. 1999. Table IB, Note 49.

(xv) OFR 00–170, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Ammonium Plus Organic Nitrogen by a Kjeldahl Digestion Method and an Automated Photometric Finish that Includes Digest Cleanup by Gas Diffusion. 2000. Table IB, Note 45.

(xvi) Techniques and Methods Book 5–B1, Determination of Elements in Natural-Water, Biota, Sediment and Soil Samples Using Collision/Reaction Cell Inductively Coupled Plasma-Mass Spectrometry. Chapter 1, Section B, Methods of the National Water Quality Laboratory, Book 5, Laboratory Analysis. 2006. Table IB, Note 70.

(xvii) U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Laboratory Analysis, Chapter A4, Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples. 1989. Table IA, Note 4; Table IH, Note 4.

(xviii) Water-Resources Investigation Report 01–4098, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Moderate-Use Pesticides and Selected Degradates in Water by C–18 Solid-Phase Extraction and Gas Chromatography/Mass Spectrometry. 2001. Table ID, Note 13.

(xix) Water-Resources Investigations Report 01–4132, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Organic Plus Inorganic Mercury in Filtered and Unfiltered Natural Water With Cold Vapor-Atomic Fluorescence Spectrometry. 2001. Table IB, Note 71.

(xx) Water-Resources Investigation Report 01–4134, Methods of Analysis by

the U.S. Geological Survey National Water Quality Laboratory—Determination of Pesticides in Water by Graphitized Carbon-Based Solid-Phase Extraction and High-Performance Liquid Chromatography/Mass Spectrometry. 2001. Table ID, Note 12.

(xxi) Water Temperature—Influential Factors, Field Measurement and Data Presentation, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 1, Chapter D1. 1975. Table IB, Note 32.

* * * * *

(c) Under certain circumstances, the Director may establish limitations on the discharge of a parameter for which there is no test procedure in this part or in 40 CFR parts 405 through 499. In these instances the test procedure shall be specified by the Director.

* * * * *

(e) * * *

TABLE II—REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Parameter number/name	Container [1]	Preservation [2 3]	Maximum holding time [4]
Table IA—Bacterial Tests:			
1–5. Coliform, total, fecal, and *E. coli*	PA, G	Cool, <10 °C, 0.008% $Na_2S_2O_3$[5].	8 hours [22 23].
6. Fecal streptococci	PA, G	Cool, <10 °C, 0.008% $Na_2S_2O_3$[5].	8 hours [22].
7. Enterococci	PA, G	Cool, <10 °C, 0.008% $Na_2S_2O_3$[5].	8 hours [22].
8. Salmonella	PA, G	Cool, <10 °C, 0.008% $Na_2S_2O_3$[5].	8 hours [22].
Table IA—Aquatic Toxicity Tests:			
9–12. Toxicity, acute and chronic	P, FP, G	Cool, ≤6 °C [16]	36 hours.
Table IB—Inorganic Tests:			
1. Acidity	P, FP, G	Cool, ≤6 °C [18]	14 days.
2. Alkalinity	P, FP, G	Cool, ≤6 °C [18]	14 days.
4. Ammonia	P, FP, G	Cool, ≤6 °C [18], H_2SO_4 to pH <2.	28 days.
9. Biochemical oxygen demand	P, FP, G	Cool, ≤6 °C [18]	48 hours.
10. Boron	P, FP, or Quartz.	HNO_3 to pH <2	6 months.
11. Bromide	P, FP, G	None required	28 days.
14. Biochemical oxygen demand, carbonaceous	P, FP G	Cool, ≤6 °C [18]	48 hours.
15. Chemical oxygen demand	P, FP, G	Cool, ≤6 °C [18], H_2SO_4 to pH <2.	28 days.
16. Chloride	P, FP, G	None required	28 days.
17. Chlorine, total residual	P, G	None required	Analyze within 15 minutes.
21. Color	P, FP, G	Cool, ≤6 °C [18]	48 hours.
23–24. Cyanide, total or available (or CATC) and free	P, FP, G	Cool, ≤6 °C [18], NaOH to pH >10 [5 6], reducing agent if oxidizer present.	14 days.
25. Fluoride	P	None required	28 days.
27. Hardness	P, FP, G	HNO_3 or H_2SO_4 to pH <2	6 months.
28. Hydrogen ion (pH)	P, FP, G	None required	Analyze within 15 minutes.
31, 43. Kjeldahl and organic N	P, FP, G	Cool, ≤6 °C [18], H_2SO_4 to pH <2.	28 days.
Table IB—Metals: [7]			
18. Chromium VI	P, FP, G	Cool, ≤6 °C [18], pH = 9.3–9.7 [20].	28 days.
35. Mercury (CVAA)	P, FP, G	HNO_3 to pH <2	28 days.
35. Mercury (CVAFS)	FP, G; and FP-lined cap [17].	5 mL/L 12N HCl or 5 mL/L BrCl [17].	90 days [17].
3, 5–8, 12, 13, 19, 20, 22, 26, 29, 30, 32–34, 36, 37, 45, 47, 51, 52, 58–60, 62, 63, 70–72, 74, 75. Metals, except boron, chromium VI, and mercury.	P, FP, G	HNO_3 to pH <2, or at least 24 hours prior to analysis [19].	6 months.
38. Nitrate	P, FP, G	Cool, ≤6 °C [18]	48 hours.
39. Nitrate-nitrite	P, FP, G	Cool, ≤6 °C [18], H_2SO_4 to pH <2.	28 days.
40. Nitrite	P, FP, G	Cool, ≤6 °C [18]	48 hours.
41. Oil and grease	G	Cool to ≤6 °C [18], HCl or H_2SO_4 to pH <2.	28 days.
42. Organic Carbon	P, FP, G	Cool to ≤6 °C [18], HCl, H_2SO_4, or H_3PO_4 to pH <2.	28 days.
44. Orthophosphate	P, FP, G	Cool, to ≤6 °C [18 24]	Filter within 15 minutes; Analyze within 48 hours.

TABLE II—REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES—Continued

Parameter number/name	Container [1]	Preservation [2 3]	Maximum holding time [4]
46. Oxygen, Dissolved Probe	G, Bottle and top.	None required	Analyze within 15 minutes.
47. Winkler	G, Bottle and top.	Fix on site and store in dark	8 hours.
48. Phenols	G	Cool, ≤6 °C [18], H_2SO_4 to pH <2.	28 days.
49. Phosphorous (elemental)	G	Cool, ≤6 °C [18]	48 hours.
50. Phosphorous, total	P, FP, G	Cool, ≤6 °C [18], H_2SO_4 to pH <2.	28 days.
53. Residue, total	P, FP, G	Cool, ≤6 °C [18]	7 days.
54. Residue, Filterable	P, FP, G	Cool, ≤6 °C [18]	7 days.
55. Residue, Nonfilterable (TSS)	P, FP, G	Cool, ≤6 °C [18]	7 days.
56. Residue, Settleable	P, FP, G	Cool, ≤6 °C [18]	48 hours.
57. Residue, Volatile	P, FP, G	Cool, ≤6 °C [18]	7 days.
61. Silica	P or Quartz	Cool, ≤6 °C [18]	28 days.
64. Specific conductance	P, FP, G	Cool, ≤6 °C [18]	28 days.
65. Sulfate	P, FP, G	Cool, ≤6 °C [18]	28 days.
66. Sulfide	P, FP, G	Cool, ≤6 °C [18], add zinc acetate plus sodium hydroxide to pH >9.	7 days.
67. Sulfite	P, FP, G	None required	Analyze within 15 minutes.
68. Surfactants	P, FP, G	Cool, ≤6 °C [18]	48 hours.
69. Temperature	P, FP, G	None required	Analyze.
73. Turbidity	P, FP, G	Cool, ≤6 °C [18]	48 hours.
Table IC—Organic Tests: [8]			
13, 18–20, 22, 24–28, 34–37, 39–43, 45–47, 56, 76, 104, 105, 108–111, 113. Purgeable Halocarbons.	G, FP-lined septum.	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$[5].	14 days.
6, 57, 106. Purgeable aromatic hydrocarbons	G, FP-lined septum.	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$[5], HCl to pH 2 [9].	14 days [9].
3, 4. Acrolein and acrylonitrile	G, FP-lined septum.	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$, pH to 4–5 [10].	14 days [10].
23, 30, 44, 49, 53, 77, 80, 81, 98, 100, 112. Phenols [11]	G, FP-lined cap.	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$.	7 days until extraction, 40 days after extraction.
7, 38. Benzidines [11 12]	G, FP-lined cap.	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$[5].	7 days until extraction [13].
14, 17, 48, 50–52. Phthalate esters [11]	G, FP-lined cap.	Cool, ≤6 °C [18]	7 days until extraction, 40 days after extraction.
82–84. Nitrosamines [11 14]	G, FP-lined cap.	Cool, ≤6 °C [18], store in dark, 0.008% $Na_2S_2O_3$[5].	7 days until extraction, 40 days after extraction.
88–94. PCBs [11]	G, FP-lined cap.	Cool, ≤6 °C [18]	1 year until extraction, 1 year after extraction.
54, 55, 75, 79. Nitroaromatics and isophorone [11]	G, FP-lined cap.	Cool, ≤6 °C [18], store in dark, 0.008% $Na_2S_2O_3$ [5].	7 days until extraction, 40 days after extraction.
1, 2, 5, 8–12, 32, 33, 58, 59, 74, 78, 99, 101. Polynuclear aromatic hydrocarbons [11].	G, FP-lined cap.	Cool, ≤6 °C [18], store in dark, 0.008% $Na_2S_2O_3$[5].	7 days until extraction, 40 days after extraction.
15, 16, 21, 31, 87. Haloethers [11]	G, FP-lined cap.	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$[5].	7 days until extraction, 40 days after extraction.
29, 35–37, 63–65, 107. Chlorinated hydrocarbons [11]	G, FP-lined cap.	Cool, ≤6 °C [18]	7 days until extraction, 40 days after extraction.
60–62, 66–72, 85, 86, 95–97, 102, 103. CDDs/CDFs [11]	G	See footnote 11	See footnote 11.
Aqueous Samples: Field and Lab Preservation	G	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$[5], pH <9.	1 year.
Solids and Mixed-Phase Samples: Field Preservation	G	Cool, ≤6 °C [18]	7 days.
Tissue Samples: Field Preservation	G	Cool, ≤6 °C [18]	24 hours.
Solids, Mixed-Phase, and Tissue Samples: Lab Preservation.	G	Freeze, ≤ −10 °C	1 year.
114–118. Alkylated phenols	G	Cool, <6 °C, H_2SO_4 to pH <2	28 days until extraction, 40 days after extraction.
119. Adsorbable Organic Halides (AOX)	G	Cool, <6 °C, 0.008% $Na_2S_2O_3$, HNO_3 to pH <2.	Hold *at least* 3 days, but not more than 6 months.
120. Chlorinated Phenolics	G, FP-lined cap.	Cool, <6 °C, 0.008% $Na_2S_2O_3$, H_2SO_4 to pH <2.	30 days until acetylation, 30 days after acetylation.
Table ID—Pesticides Tests:			
1–70. Pesticides [11]	G, FP-lined cap.	Cool, ≤6 °C [18], pH 5–9 [15]	7 days until extraction, 40 days after extraction.

TABLE II—REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES—Continued

Parameter number/name	Container [1]	Preservation [2 3]	Maximum holding time [4]
Table IE—Radiological Tests:			
1–5. Alpha, beta, and radium	P, FP, G	HNO_3 to pH <2	6 months.
Table IH—Bacterial Tests:			
1–4. Coliform, total, fecal	PA, G	Cool, <10 °C, 0.008% $Na_2S_2O_3$[5].	8 hours [22 23].
5. *E. coli*	PA, G	Cool, <10 °C, 0.008% $Na_2S_2O_3$[5].	8 hours [22].
6. Fecal streptococci	PA, G	Cool, <10 °C, 0.008% $Na_2S_2O_3$[5].	8 hours [22].
7. Enterococci	PA, G	Cool, <10 °C, 0.008% $Na_2S_2O_3$[5].	8 hours [22].
Table IH—Protozoan Tests:			
8. Cryptosporidium	LDPE; field filtration.	1–10 °C	96 hours [21].
9. Giardia	LDPE; field filtration.	1–10 °C	96 hours [21].

[1] "P" is for polyethylene; "FP" is fluoropolymer (polytetrafluoroethylene (PTFE); Teflon®), or other fluoropolymer, unless stated otherwise in this Table II; "G" is glass; "PA" is any plastic that is made of a sterilizable material (polypropylene or other autoclavable plastic); "LDPE" is low density polyethylene.

[2] Except where noted in this Table II and the method for the parameter, preserve each grab sample within 15 minutes of collection. For a composite sample collected with an automated sample (*e.g.,* using a 24-hour composite sample; see 40 CFR 122.21(g)(7)(i) or 40 CFR part 403, appendix E), refrigerate the sample at ≤ 6 °C during collection unless specified otherwise in this Table II or in the method(s). For a composite sample to be split into separate aliquots for preservation and/or analysis, maintain the sample at ≤ 6 °C, unless specified otherwise in this Table II or in the method(s), until collection, splitting, and preservation is completed. Add the preservative to the sample container prior to sample collection when the preservative will not compromise the integrity of a grab sample, a composite sample, or aliquot split from a composite sample within 15 minutes of collection. If a composite measurement is required but a composite sample would compromise sample integrity, individual grab samples must be collected at prescribed time intervals (*e.g.,* 4 samples over the course of a day, at 6-hour intervals). Grab samples must be analyzed separately and the concentrations averaged. Alternatively, grab samples may be collected in the field and composited in the laboratory if the compositing procedure produces results equivalent to results produced by arithmetic averaging of results of analysis of individual grab samples. For examples of laboratory compositing procedures, see EPA Method 1664 Rev. A (oil and grease) and the procedures at 40 CFR 141.24(f)(14)(iv) and (v) (volatile organics).

[3] When any sample is to be shipped by common carrier or sent via the U.S. Postal Service, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirement of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater; Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

[4] Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before the start of analysis and still be considered valid. Samples may be held for longer periods only if the permittee or monitoring laboratory have data on file to show that, for the specific types of samples under study, the analytes are stable for the longer time, and has received a variance from the Regional ATP Coordinator under § 136.3(e). For a grab sample, the holding time begins at the time of collection. For a composite sample collected with an automated sampler (*e.g.,* using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR part 403, appendix E), the holding time begins at the time of the end of collection of the composite sample. For a set of grab samples composited in the field or laboratory, the holding time begins at the time of collection of the last grab sample in the set. Some samples may not be stable for the maximum time period given in the table. A permittee or monitoring laboratory is obligated to hold the sample for a shorter time if it knows that a shorter time is necessary to maintain sample stability. See § 136.3(e) for details. The date and time of collection of an individual grab sample is the date and time at which the sample is collected. For a set of grab samples to be composited, and that are all collected on the same calendar date, the date of collection is the date on which the samples are collected. For a set of grab samples to be composited, and that are collected across two calendar dates, the date of collection is the dates of the two days; *e.g.,* November 14–15. For a composite sample collected automatically on a given date, the date of collection is the date on which the sample is collected. For a composite sample collected automatically, and that is collected across two calendar dates, the date of collection is the dates of the two days; *e.g.,* November 14–15. For static-renewal toxicity tests, each grab or composite sample may also be used to prepare test solutions for renewal at 24 h, 48 h, and/or 72 h after first use, if stored at 0–6 °C, with minimum head space.

[5] ASTM D7365–09a specifies treatment options for samples containing oxidants (*e.g.,* chlorine) for cyanide analyses. Also, Section 9060A of Standard Methods for the Examination of Water and Wastewater (20th and 21st editions) addresses dechlorination procedures for microbiological analyses.

[6] Sampling, preservation and mitigating interferences in water samples for analysis of cyanide are described in ASTM D7365–09a. There may be interferences that are not mitigated by the analytical test methods or D7365–09a. Any technique for removal or suppression of interference may be employed, provided the laboratory demonstrates that it more accurately measures cyanide through quality control measures described in the analytical test method. Any removal or suppression technique not described in D7365–09a or the analytical test method must be documented along with supporting data.

[7] For dissolved metals, filter grab samples within 15 minutes of collection and before adding preservatives. For a composite sample collected with an automated sampler (*e.g.,* using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR part 403, appendix E), filter the sample within 15 minutes after completion of collection and before adding preservatives. If it is known or suspected that dissolved sample integrity will be compromised during collection of a composite sample collected automatically over time (*e.g.,* by interchange of a metal between dissolved and suspended forms), collect and filter grab samples to be composited (footnote 2) in place of a composite sample collected automatically.

[8] Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.

[9] If the sample is not adjusted to pH 2, then the sample must be analyzed within seven days of sampling.

[10] The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.

[11] When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity (*i.e.,* use all necessary preservatives and hold for the shortest time listed). When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to ≤ 6 °C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6–9; samples preserved in this manner may be held for seven days before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (regarding the requirement for thiosulfate reduction), and footnotes 12, 13 (regarding the analysis of benzidine).

[12] If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0 ± 0.2 to prevent rearrangement to benzidine.

[13] Extracts may be stored up to 30 days at < 0 °C.

[14] For the analysis of diphenylnitrosamine, add 0.008% $Na_2S_2O_3$ and adjust pH to 7–10 with NaOH within 24 hours of sampling.

[15] The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% $Na_2S_2O_3$.

[16] Place sufficient ice with the samples in the shipping container to ensure that ice is still present when the samples arrive at the laboratory. However, even if ice is present when the samples arrive, immediately measure the temperature of the samples and confirm that the preservation temperature maximum has not been exceeded. In the isolated cases where it can be documented that this holding temperature cannot be met, the permittee can be given the option of on-site testing or can request a variance. The request for a variance should include supportive data which show that the toxicity of the effluent samples is not reduced because of the increased holding temperature. Aqueous samples must not be frozen. Hand-delivered samples used on the day of collection do not need to be cooled to 0 to 6 °C prior to test initiation.

[17] Samples collected for the determination of trace level mercury (<100 ng/L) using EPA Method 1631 must be collected in tightly-capped fluoropolymer or glass bottles and preserved with BrCl or HCl solution within 48 hours of sample collection. The time to preservation may be extended to 28 days if a sample is oxidized in the sample bottle. A sample collected for dissolved trace level mercury should be filtered in the laboratory within 24 hours of the time of collection. However, if circumstances preclude overnight shipment, the sample should be filtered in a designated clean area in the field in accordance with procedures given in Method 1669. If sample integrity will not be maintained by shipment to and filtration in the laboratory, the sample must be filtered in a designated clean area in the field within the time period necessary to maintain sample integrity. A sample that has been collected for determination of total or dissolved trace level mercury must be analyzed within 90 days of sample collection.

[18] Aqueous samples must be preserved at ≤ 6 °C, and should not be frozen unless data demonstrating that sample freezing does not adversely impact sample integrity is maintained on file and accepted as valid by the regulatory authority. Also, for purposes of NPDES monitoring, the specification of "≤ °C" is used in place of the "4 °C" and "< 4 °C" sample temperature requirements listed in some methods. It is not necessary to measure the sample temperature to three significant figures (1/100th of 1 degree); rather, three significant figures are specified so that rounding down to 6 °C may not be used to meet the ≤6 °C requirement. The preservation temperature does not apply to samples that are analyzed immediately (less than 15 minutes).

[19] An aqueous sample may be collected and shipped without acid preservation. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. If the sample must be analyzed within 24 hours of collection, add the acid immediately (see footnote 2). Soil and sediment samples do not need to be preserved with acid. The allowances in this footnote supersede the preservation and holding time requirements in the approved metals methods.

[20] To achieve the 28-day holding time, use the ammonium sulfate buffer solution specified in EPA Method 218.6. The allowance in this footnote supersedes preservation and holding time requirements in the approved hexavalent chromium methods, unless this supersession would compromise the measurement, in which case requirements in the method must be followed.

[21] Holding time is calculated from time of sample collection to elution for samples shipped to the laboratory in bulk and calculated from the time of sample filtration to elution for samples filtered in the field.

[22] Sample analysis should begin as soon as possible after receipt; sample incubation must be started no later than 8 hours from time of collection.

[23] For fecal coliform samples for sewage sludge (biosolids) only, the holding time is extended to 24 hours for the following sample types using either EPA Method 1680 (LTB–EC) or 1681 (A–1): Class A composted, Class B aerobically digested, and Class B anaerobically digested.

[24] The immediate filtration requirement in orthophosphate measurement is to assess the dissolved or bio-available form of orthophosphorus (*i.e.,* that which passes through a 0.45-micron filter), hence the requirement to filter the sample immediately upon collection (*i.e.,* within 15 minutes of collection).

■ 5. Section 136.4 is amended by revising paragraphs (a) introductory text, (b), and (c) to read as follows:

§ 136.4 Application for and approval of alternate test procedures for nationwide use.

(a) A written application for review of an alternate test procedure (alternate method) for nationwide use may be made by letter via email or by hard copy in triplicate to the National Alternate Test Procedure (ATP) Program Coordinator (National Coordinator), Office of Science and Technology (4303T), Office of Water, U.S. Environmental Protection Agency, 1200 Pennsylvania Ave. NW., Washington, DC 20460. Any application for an ATP under this paragraph (a) shall:

* * * * *

(b) The National Coordinator may request additional information and analyses from the applicant in order to evaluate whether the alternate test procedure satisfies the applicable requirements of this part.

(c) *Approval for nationwide use.* (1) After a review of the application and any additional analyses requested from the applicant, the National Coordinator will notify the applicant, in writing, of whether the National Coordinator will recommend approval or disapproval of the alternate test procedure for nationwide use in CWA programs. If the application is not recommended for approval, the National Coordinator may specify what additional information might lead to a reconsideration of the application and notify the Regional Alternate Test Procedure Coordinators of the disapproval recommendation. Based on the National Coordinator's recommended disapproval of a proposed alternate test procedure and an assessment of any current approvals for limited uses for the unapproved method, the Regional ATP Coordinator may decide to withdraw approval of the method for limited use in the Region.

(2) Where the National Coordinator has recommended approval of an applicant's request for nationwide use of an alternate test procedure, the National Coordinator will notify the applicant. The National Coordinator will also notify the Regional ATP Coordinators that they may consider approval of this alternate test procedure for limited use in their Regions based on the information and data provided in the application until the alternate test procedure is approved by publication in a final rule in the **Federal Register**.

(3) EPA will propose to amend this part to include the alternate test procedure in § 136.3. EPA shall make available for review all the factual bases for its proposal, including the method, any performance data submitted by the applicant and any available EPA analysis of those data.

(4) Following public comment, EPA shall publish in the **Federal Register** a final decision on whether to amend this part to include the alternate test procedure as an approved analytical method for nationwide use.

(5) Whenever the National Coordinator has recommended approval of an applicant's ATP request for nationwide use, any person may request an approval of the method for limited use under § 136.5 from the EPA Region.

■ 6. Section 136.5 is amended by revising paragraphs (a), (b), (c)(1), and (d) to read as follows:

§ 136.5 Approval of alternate test procedures for limited use.

(a) Any person may request the Regional ATP Coordinator to approve the use of an alternate test procedure in the Region.

(b) When the request for the use of an alternate test procedure concerns use in a State with an NPDES permit program approved pursuant to section 402 of the Act, the requestor shall first submit an application for limited use to the Director of the State agency having responsibility for issuance of NPDES permits within such State (*i.e.,* permitting authority). The Director will forward the application to the Regional ATP Coordinator with a recommendation for or against approval.

(c) * * *

(1) Provide the name and address of the applicant and the applicable ID number of the existing or pending permit(s) and issuing agency for which use of the alternate test procedure is requested, and the discharge serial number.

* * * * *

(d) *Approval for limited use.* (1) The Regional ATP Coordinator will review the application and notify the applicant and the appropriate State agency of approval or rejection of the use of the alternate test procedure. The approval may be restricted to use only with respect to a specific discharge or facility (and its laboratory) or, at the discretion of the Regional ATP Coordinator, to all dischargers or facilities (and their associated laboratories) specified in the approval for the Region. If the application is not approved, the Regional ATP Coordinator shall specify what additional information might lead to a reconsideration of the application.

(2) The Regional ATP Coordinator will forward a copy of every approval and rejection notification to the National Alternate Test Procedure Coordinator.

■ 7. In § 136.6:

■ a. Revise paragraphs (b)(1) and (2) introductory text.

■ b. Remove paragraph (b)(4)(xvi).

■ c. Redesignate paragraphs (b)(4)(xvii) through (xxii) as paragraphs (b)(4)(xvi) through (xxi), respectively.

■ d. Add paragraph (c).

The revision and addition read as follows:

§ 136.6 Method modifications and analytical requirements.

* * * * *

(b) *Method modifications.* (1) If the underlying chemistry and determinative technique in a modified method are essentially the same as an approved part 136 method, then the modified method is an equivalent and acceptable alternative to the approved method provided the requirements of this section are met. However, those who develop or use a modification to an approved (part 136) method must document that the performance of the modified method, in the matrix to which the modified method will be applied, is equivalent to the performance of the approved method. If such a demonstration cannot be made and documented, then the modified method is not an acceptable alternative to the approved method. Supporting documentation must, if applicable, include the routine initial demonstration of capability and ongoing QC including determination of precision and accuracy, detection limits, and matrix spike recoveries. Initial demonstration of capability typically includes analysis of four replicates of a mid-level standard and a method detection limit study. Ongoing quality control typically includes method blanks, mid-level laboratory control samples, and matrix spikes (QC is as specified in the method). The method is considered equivalent if the quality control requirements in the reference method are achieved. The method user's Standard Operating Procedure (SOP) must clearly document the modifications made to the reference method. Examples of allowed method modifications are listed in this section. If the method user is uncertain whether a method modification is allowed, the Regional ATP Coordinator or Director should be contacted for approval *prior* to implementing the modification. The method user should also complete necessary performance checks to verify that acceptable performance is achieved with the method modification *prior* to analyses of compliance samples.

(2) *Requirements.* The modified method must meet or exceed performance of the approved method(s) for the analyte(s) of interest, as documented by meeting the initial and ongoing quality control requirements in the method.

* * * * *

(c) The permittee must notify their permitting authority of the intent to use a modified method. Such notification should be of the form ''Method xxx has been modified within the flexibility allowed in 40 CFR 136.6.'' The permittee may indicate the specific paragraph of § 136.6 allowing the method modification. Specific details of the modification need not be provided, but must be documented in the Standard Operating Procedure (SOP) and maintained by the analytical laboratory that performs the analysis.

■ 8. In Appendix A to part 136:

■ a. Revise Method 608.

■ b. Revise Method 611, section 1.1.

■ c. Revise Method 624.

■ d. Revise Method 625.

The revisions read as follows:

Appendix A to Part 136—Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater

* * * * *

Method 608.3—Organochlorine Pesticides And PCBs By GC/HSD

1. Scope and Application

1.1 This method is for determination of organochlorine pesticides and polychlorinated biphenyls (PCBs) in industrial discharges and other environmental samples by gas chromatography (GC) combined with a halogen-specific detector (HSD; *e.g.,* electron capture, electrolytic conductivity), as provided under 40 CFR 136.1. This revision is based on a previous protocol (Reference 1), on the revision promulgated October 26, 1984 (49 FR 43234), on an inter-laboratory method validation study (Reference 2), and on EPA Method 1656 (Reference 16). The analytes that may be qualitatively and quantitatively determined using this method and their CAS Registry numbers are listed in Table 1.

1.2 This method may be extended to determine the analytes listed in Table 2. However, extraction or gas chromatography challenges for some of these analytes may make quantitative determination difficult.

1.3 When this method is used to analyze unfamiliar samples for an analyte listed in Table 1 or Table 2, analyte identification must be supported by at least one additional qualitative technique. This method gives analytical conditions for a second GC column that can be used to confirm and quantify measurements.

Additionally, Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative confirmation of results for the analytes listed in Tables 1 and 2 using the extract produced by this method, and Method 1699 (Reference 18) provides high resolution GC/MS conditions for qualitative confirmation of results using the original sample. When such methods are used to confirm the identifications of the target analytes, the quantitative results should be derived from the procedure with the

calibration range and sensitivity that are most appropriate for the intended application.

1.4 The large number of analytes in Tables 1 and 2 makes testing difficult if all analytes are determined simultaneously. Therefore, it is necessary to determine and perform quality control (QC) tests for the ''analytes of interest'' only. The analytes of interest are those required to be determined by a regulatory/control authority or in a permit, or by a client. If a list of analytes is not specified, the analytes in Table 1 must be determined, at a minimum, and QC testing must be performed for these analytes. The analytes in Table 1 and some of the analytes in Table 2 have been identified as Toxic Pollutants (40 CFR 401.15), expanded to a list of Priority Pollutants (40 CFR part 423, appendix A).

1.5 In this revision to Method 608, Chlordane has been listed as the alpha- and gamma-isomers in Table 1. Reporting may be by the individual isomers, or as the sum of the concentrations of these isomers, as requested or required by a regulatory/control authority or in a permit. Technical Chlordane is listed in Table 2 and may be used in cases where historical reporting has only been the Technical Chlordane. Toxaphene and the PCBs have been moved from Table 1 to Table 2 (Additional Analytes) to distinguish these analytes from the analytes required in quality control tests (Table 1). QC acceptance criteria for Toxaphene and the PCBs have been retained in Table 4 and may continue to be applied if desired, or if these analytes are requested or required by a regulatory/control authority or in a permit. Method 1668C (Reference 17) may be useful for determination of PCBs as individual chlorinated biphenyl congeners, and Method 1699 (Reference 18) may be useful for determination of the pesticides listed in this method. However, at the time of writing of this revision, Methods 1668C and 1699 had not been approved for use at 40 CFR part 136.

1.6 Method detection limits (MDLs; Reference 3) for the analytes in Tables 1 and some of the analytes in Table 2 are listed in those tables. These MDLs were determined in reagent water (Reference 3). Advances in analytical technology, particularly the use of capillary (open-tubular) columns, allowed laboratories to routinely achieve MDLs for the analytes in this method that are 2–10 times lower than those in the version promulgated in 1984 (40 FR 43234). The MDL for an analyte in a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.6.1 EPA has promulgated this method at 40 CFR part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described in Section 15.2 are focused on such monitoring needs and may not be relevant to other uses of the method.

1.6.2 This method includes ''reporting limits'' based on EPA's ''minimum level'' (ML) concept (see the glossary in Section 23). Tables 1 and 2 contain MDL values and ML values for many of the analytes. The MDL for an analyte in a specific wastewater may differ from those listed in Tables 1 or 2, depending upon the nature of interferences in the sample matrix.

1.7 The separatory funnel and continuous liquid-liquid sample extraction and concentration steps in this method are essentially the same as those steps in Methods 606, 609, 611, and 612. Thus, a single sample may be extracted to measure the analytes included in the scope of each of these methods. Samples may also be extracted using a disk-based solid-phase extraction (SPE) procedure developed by the 3M Corporation and approved by EPA as an Alternate Test Procedure (ATP) for wastewater analyses in 1995 (Reference 20).

1.8 This method is performance-based. It may be modified to improve performance (*e.g.,* to overcome interferences or improve the accuracy of results) provided all performance requirements are met.

1.8.1 Examples of allowed method modifications are described at 40 CFR 136.6. Other examples of allowed modifications specific to this method are described in Section 8.1.2.

1.8.2 Any modification beyond those expressly permitted at 40 CFR 136.6 or in Section 8.1.2 of this method shall be considered a major modification subject to application and approval of an alternate test procedure under 40 CFR 136.4 and 136.5.

1.8.3 For regulatory compliance, any modification must be demonstrated to produce results equivalent or superior to results produced by this method when applied to relevant wastewaters (Section 8.1.2).

1.9 This method is restricted to use by or under the supervision of analysts experienced in the use of GC/HSD. The laboratory must demonstrate the ability to generate acceptable results with this method using the procedure in Section 8.2.

1.10 Terms and units of measure used in this method are given in the glossary at the end of the method.

2. Summary of Method

2.1 A measured volume of sample, the amount required to meet an MDL or reporting limit (nominally 1–L), is extracted with methylene chloride using a separatory funnel, a continuous liquid/liquid extractor, or disk-based solid-phase extraction equipment. The extract is dried and concentrated for cleanup, if required. After cleanup, or if cleanup is not required, the extract is exchanged into an appropriate solvent and concentrated to the volume necessary to meet the required compliance or detection limit, and analyzed by GC/HSD.

2.2 Qualitative identification of an analyte in the extract is performed using the retention times on dissimilar GC columns. Quantitative analysis is performed using the peak areas or peak heights for the analyte on the dissimilar columns with either the external or internal standard technique.

2.3 Florisil®, alumina, a C18 solid-phase cleanup, and an elemental sulfur cleanup procedure are provided to aid in elimination of interferences that may be encountered. Other cleanup procedures may be used if demonstrated to be effective for the analytes in a wastewater matrix.

3. Contamination and Interferences

3.1 Solvents, reagents, glassware, and other sample processing lab ware may yield artifacts, elevated baselines, or matrix interferences causing misinterpretation of chromatograms. All materials used in the analysis must be demonstrated free from contamination and interferences by running blanks initially and with each extraction batch (samples started through the extraction process in a given 24-hour period, to a maximum of 20 samples). Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, lab ware is cleaned by extraction or solvent rinse, or baking in a kiln or oven. All materials used must be routinely demonstrated to be free from interferences under the conditions of the analysis by running blanks as described in Section 8.5.

3.2 Glassware must be scrupulously cleaned (Reference 4). Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and reagent water. The glassware should then be drained dry, and heated at 400 °C for

15–30 minutes. Some thermally stable materials, such as PCBs, may require higher temperatures and longer baking times for removal. Solvent rinses with pesticide quality acetone, hexane, or other solvents may be substituted for heating. Volumetric lab ware should not be heated excessively or for long periods of time. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.3 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. The phthalate esters generally appear in the chromatogram as large late eluting peaks, especially in the 15 and 50% fractions from Florisil®. Common flexible plastics contain varying amounts of phthalates that may be extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding use of non-fluoropolymer plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination (References 5 and 6). Interferences from phthalate esters can be avoided by using a microcoulometric or electrolytic conductivity detector.

3.4 Matrix interferences may be caused by contaminants co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. Interferences extracted from samples high in total organic carbon (TOC) may result in elevated baselines, or by enhancing or suppressing a signal at or near the retention time of an analyte of interest. Analyses of the matrix spike and duplicate (Section 8.3) may be useful in identifying matrix interferences, and the cleanup procedures in Section 11 may aid in eliminating these interferences. EPA has provided guidance that may aid in overcoming matrix interferences (Reference 7); however, unique samples may require additional cleanup approaches to achieve the MDLs listed in Table 3.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of safety data sheets (SDSs, OSHA, 29 CFR 1910.1200(g)) should also be made available to all personnel involved in sample handling and chemical analysis. Additional references to laboratory safety are available and have been identified (References 8 and 9) for the information of the analyst.

4.2 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: 4,4′-DDT, 4,4′-DDD, the BHCs, and the PCBs. Primary standards of these toxic analytes should be prepared in a chemical fume hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations are handled.

4.3 This method allows the use of hydrogen as a carrier gas in place of helium (Section 5.8.2). The laboratory should take the necessary precautions in dealing with hydrogen, and should limit hydrogen flow at the source to prevent buildup of an explosive mixture of hydrogen in air.

5. Apparatus and Materials

Note: Brand names and suppliers are for illustration purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here. Demonstrating that the equipment and supplies used in the laboratory achieve the required performance is the responsibility of the laboratory. Suppliers for equipment and materials in this method may be found through an on-line search. Please do not contact EPA for supplier information.

5.1 Sampling equipment, for discrete or composite sampling

5.1.1 Grab sample bottle—amber glass bottle large enough to contain the necessary sample volume (nominally 1 L), fitted with a fluoropolymer-lined screw cap. Foil may be substituted for fluoropolymer if the sample is not corrosive. If amber bottles are not available, protect samples from light. Unless pre-cleaned, the bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—the sampler must use a glass or fluoropolymer container and tubing for sample collection. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsing with reagent water to minimize the potential for sample contamination. An integrating flow meter is required to collect flow proportional composites. The sample container must be kept refrigerated at <6 °C and protected from light during compositing.

5.2. Lab ware

5.2.1 Extraction

5.2.1.1 pH measurement

5.2.1.1.1 pH meter, with combination glass electrode

5.2.1.1.2 pH paper, wide range (Hydrion Papers, or equivalent)

5.2.1.2 Separatory funnel—Size appropriate to hold the sample and extraction solvent volumes, equipped with fluoropolymer stopcock.

5.2.1.3 Continuous liquid-liquid extractor—Equipped with fluoropolymer or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, NJ, or equivalent.)

5.2.1.3.1 Round-bottom flask, 500-mL, with heating mantle

5.2.1.3.2 Condenser, Graham, to fit extractor

5.2.1.4 Solid-phase extractor—90-mm filter apparatus (Figure 2) or multi-position manifold

5.2.1.4.1 Vacuum system—Capable of achieving 0.1 bar (25 inch) Hg (house vacuum, vacuum pump, or water aspirator), equipped with shutoff valve and vacuum gauge

5.2.1.4.2 Vacuum trap—Made from 500-mL sidearm flask fitted with single-hole rubber stopper and glass tubing

Note: The approved ATP for solid-phase extraction is limited to disk-based extraction media and associated peripheral equipment.

5.2.2 Filtration

5.2.2.1 Glass powder funnel, 125- to 250-mL

5.2.2.2 Filter paper for above, Whatman 41, or equivalent

5.2.2.3 Prefiltering aids—90-mm 1-µm glass fiber filter or Empore® Filter Aid 400

5.2.3 Drying column

5.2.3.1 Chromatographic column—approximately 400 mm long × 15 mm ID, with fluoropolymer stopcock and coarse frit filter disc (Kontes or equivalent).

5.2.3.2 Glass wool—Pyrex, extracted with methylene chloride or baked at 450 °C for 1 hour minimum

5.2.4 Column for Florisil® or alumina cleanup—approximately 300

mm long × 10 mm ID, with fluoropolymer stopcock. (This column is not required if cartridges containing Florisil® are used.)

5.2.5 Concentration/evaporation

Note: Use of a solvent recovery system with the K–D or other solvent evaporation apparatus is strongly recommended.

5.2.5.1 Kuderna-Danish concentrator

5.2.5.1.1 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes or equivalent). Calibration must be checked at the volumes employed for extract volume measurement. A ground-glass stopper is used to prevent evaporation of extracts.

5.2.5.1.2 Evaporative flask, Kuderna-Danish—500-mL (Kontes or equivalent). Attach to concentrator tube with connectors.

5.2.5.1.3 Snyder column, Kuderna/Danish—Three-ball macro (Kontes or equivalent)

5.2.5.1.4 Snyder column—Two-ball micro (Kontes or equivalent)

5.2.5.1.5 Water bath—Heated, with concentric ring cover, capable of temperature control (± 2 °C), installed in a hood using appropriate engineering controls to limit exposure to solvent vapors.

5.2.5.2 Nitrogen evaporation device—Equipped with heated bath that can be maintained at an appropriate temperature for the solvent and analytes. (N-Evap, Organomation Associates, Inc., or equivalent)

5.2.5.3 Rotary evaporator—Buchi/Brinkman-American Scientific or equivalent, equipped with a variable temperature water bath, vacuum source with shutoff valve at the evaporator, and vacuum gauge.

5.2.5.2.1 A recirculating water pump and chiller are recommended, as use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance as water temperatures and pressures vary.

5.2.5.2.2 Round-bottom flask—100-mL and 500-mL or larger, with ground-glass fitting compatible with the rotary evaporator

Note: This equipment is used to prepare copper foil or copper powder for removing sulfur from sample extracts (see Section 6.7.4).

5.2.5.4 Automated concentrator—Equipped with glassware sufficient to concentrate 3–400 mL extract to a final volume of 1–10 mL under controlled conditions of temperature and nitrogen flow (Turbovap, or equivalent). Follow manufacturer's directions and requirements.

5.2.5.5 Boiling chips—Glass, silicon carbide, or equivalent, approximately 10/40 mesh. Heat at 400 °C for 30 minutes, or solvent rinse or Soxhlet extract with methylene chloride.

5.2.5 Solid-phase extraction disks—90-mm extraction disks containing 2 g of 8-µm octadecyl (C18) bonded silica uniformly enmeshed in a matrix of inert PTFE fibrils (3M Empore® or equivalent). The disks should not contain any organic compounds, either from the PTFE or the bonded silica, which will leach into the methylene chloride eluant. One liter of reagent water should pass through the disks in 2–5 minutes, using a vacuum of at least 25 inches of mercury.

Note: Extraction disks from other manufacturers may be used in this procedure, provided that they use the same solid phase materials (*i.e.,* octadecyl bonded silica). Disks of other diameters also may be used, but may adversely affect the flow rate of the sample through the disk.

5.3 Vials

5.3.1 Extract storage—10- to 15-mL, amber glass, with fluoropolymer-lined screw cap

5.3.2 GC autosampler—1- to 5-mL, amber glass, with fluoropolymer-lined screw- or crimp-cap, to fit GC autosampler

5.4 Balances

5.4.1 Analytical—capable of accurately weighing 0.1 mg

5.4.2 Top loading—capable of weighing 10 mg

5.5 Sample cleanup

5.5.1 Oven—For baking and storage of adsorbents, capable of maintaining a constant temperature (± 5 °C) in the range of 105–250 °C.

5.5.2 Muffle furnace—Capable of cleaning glassware or baking sodium sulfate in the range of 400–450 °C.

5.5.3 Vacuum system and cartridges for solid-phase cleanup (see Section 11.2)

5.5.3.1 Vacuum system—Capable of achieving 0.1 bar (25 in.) Hg (house vacuum, vacuum pump, or water aspirator), equipped with shutoff valve and vacuum gauge

5.5.3.2 VacElute Manifold (Analytichem International, or equivalent)

5.5.3.3 Vacuum trap—Made from 500-mL sidearm flask fitted with single-hole rubber stopper and glass tubing

5.5.3.4 Rack for holding 50-mL volumetric flasks in the manifold

5.5.3.5 Cartridge—Mega Bond Elute, Non-polar, C18 Octadecyl, 10 g/60 mL (Analytichem International or equivalent), used for solid-phase cleanup of sample extracts (see Section 11.2)

5.5.3.5.1 Cartridge certification—Each cartridge lot must be certified to ensure recovery of the analytes of interest and removal of 2,4,6-trichlorophenol. To make the test mixture, add the trichlorophenol solution (Section 6.7.2.1) to the same standard used to prepare the Quality Control Check Sample (Section 6.8.3). Transfer the mixture to the column and dry the column. Pre-elute with three 10-mL portions of elution solvent, drying the column between elutions. Elute the cartridge with 10 mL each of methanol and water, as in Section 11.2.3.3.

5.5.3.5.2 Concentrate the eluant to per Section 10.3.3, exchange to isooctane or hexane per Section 10.3.3, and inject 1.0 µL of the concentrated eluant into the GC using the procedure in Section 12. The recovery of all analytes (including the unresolved GC peaks) shall be within the ranges for calibration verification (Section 13.6 and Table 4), and the peak for trichlorophenol shall not be detectable; otherwise the SPE cartridge is not performing properly and the cartridge lot shall be rejected.

5.5.4 Sulfur removal tube—40- to 50-mL bottle, test tube, or Erlenmeyer flask with fluoropolymer-lined screw cap

5.6 Centrifuge apparatus

5.6.1 Centrifuge—Capable of rotating 500-mL centrifuge bottles or 15-mL centrifuge tubes at 5,000 rpm minimum

5.6.2 Centrifuge bottle—500-mL, with screw cap, to fit centrifuge

5.6.3 Centrifuge tube—15-mL, with screw cap, to fit centrifuge

5.7 Miscellaneous lab ware—graduated cylinders, pipettes, beakers, volumetric flasks, vials, syringes, and other lab ware necessary to support the operations in this method

5.8 Gas chromatograph—Dual-column with simultaneous split/splitless, temperature programmable split/splitless (PTV), or on-column injection; temperature program with isothermal holds, and all required accessories including syringes, analytical columns, gases, and detectors. An autosampler is highly recommended because it injects volumes more reproducibly than manual injection techniques. Alternatively, two separate single-column gas chromatographic systems may be employed.

5.8.1 Example columns and operating conditions

5.8.1.1 DB–608 (or equivalent), 30-m long × 0.53-mm ID fused-silica capillary, 0.83-µm film thickness.

5.8.1.2 DB–1701 (or equivalent), 30-m long × 0.53-mm ID fused-silica capillary, 1.0-µm film thickness.

5.8.1.3 Suggested operating conditions used to meet the retention times shown in Table 3 are:

Carrier gas flow rate: approximately 7 mL/min

Initial temperature: 150 °C for 0.5 minute,
Temperature program: 150–270 °C at 5 °C/min, and
Final temperature: 270 °C, until trans-Permethrin elutes

Note: Other columns, internal diameters, film thicknesses, and operating conditions may be used, provided that the performance requirements in this method are met. However, the column pair chosen must have dissimilar phases/chemical properties in order to separate the compounds of interest in different retention time order. Columns that only differ in the length, ID, or film thickness, but use the same stationary phase do not qualify as ''dissimilar.''

5.8.2 Carrier gas—Helium or hydrogen. Data in the tables in this method were obtained using helium carrier gas. If hydrogen is used, analytical conditions may need to be adjusted for optimum performance, and calibration and all QC tests must be performed with hydrogen carrier gas. See Section 4.3 for precautions regarding the use of hydrogen as a carrier gas.

5.8.3 Detector—Halogen-specific detector (electron capture detector (ECD), electrolytic conductivity detector (ELCD), or equivalent). The ECD has proven effective in the analysis of wastewaters for the analytes listed in Tables 1 and 2, and was used to develop the method performance data in Section 17 and Tables 4 and 5.

5.8.4 Data system—A computer system must be interfaced to the GC that allows continuous acquisition and storage of data from the detectors throughout the chromatographic program. The computer must have software that allows searching GC data for specific analytes, and for plotting responses versus time. Software must also be available that allows integrating peak areas or peak heights in selected retention time windows and calculating concentrations of the analytes.

6. Reagents and Standards

6.1 pH adjustment

6.1.1 Sodium hydroxide solutions

6.1.1.1 Concentrated (10 M)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.1.1.2 Dilute (1 M)—Dissolve 40 g NaOH in 1 L of reagent water.

6.1.2 Sulfuric acid (1 + 1)—Slowly add 50 mL of H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.1.3 Hydrochloric acid—Reagent grade, 6 N

6.2 Sodium thiosulfate—(ACS) granular.

6.3 Sodium sulfate—Sodium sulfate, reagent grade, granular anhydrous (Baker or equivalent), rinsed with methylene chloride (20 mL/g), baked in a shallow tray at 450 °C for 1 hour minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw cap which prevents moisture from entering. If, after heating, the sodium sulfate develops a noticeable grayish cast (due to the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Extraction with methylene chloride (as opposed to simple rinsing) and baking at a lower temperature may produce sodium sulfate suitable for use.

6.4 Reagent water—Reagent water is defined as water in which the analytes of interest and interfering compounds are not observed at the MDLs of the analytes in this method.

6.5 Solvents—methylene chloride, acetone, methanol, hexane, acetonitrile, and isooctane, high purity pesticide quality, or equivalent, demonstrated to be free of the analytes and interferences (Section 3). Purification of solvents by distillation in all-glass systems may be required.

Note: The standards and final sample extracts must be prepared in the same final solvent.

6.6 Ethyl ether—Nanograde, redistilled in glass if necessary

Ethyl ether must be shown to be free of peroxides before use, as indicated by EM Laboratories Quant test strips (available from Scientific Products Co. and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips. After removal of peroxides, add 20 mL of ethyl alcohol preservative to each liter of ether.

6.7 Materials for sample cleanup

6.7.1 Florisil®—PR grade (60/100 mesh), activated at 650—700 °C, stored in the dark in a glass container with fluoropolymer-lined screw cap. Activate each batch immediately prior to use for 16 hours minimum at 130 °C in a foil-covered glass container and allow to cool. Alternatively, 500 mg cartridges (J.T. Baker, or equivalent) may be used.

6.7.2 Solutions for solid-phase cleanup

6.7.2.1 SPE cartridge calibration solution—2,4,6-trichlorophenol, 0.1 µg/mL in acetone.

6.7.2.2 SPE elution solvent—methylene chloride:acetonitrile:hexane (50:3:47).

6.7.3 Alumina, neutral, Brockman Activity I, 80–200 mesh (Fisher Scientific certified, or equivalent). Heat in a glass bottle for 16 hours at 400 to 450 °C. Seal and cool to room temperature. Add 7% (w/w) reagent water and mix for 10 to 12 hours. Keep bottle tightly sealed.

6.7.4 Sulfur removal

6.7.4.1 Copper foil or powder—Fisher, Alfa Aesar, or equivalent. Cut copper foil into approximately 1-cm squares. Copper must be activated on each day it will be used, as described below.

6.7.4.1.1 Place the quantity of copper needed for sulfur removal (Section 11.5.1.3) in a ground-glass-stoppered Erlenmeyer flask or bottle. Cover the foil or powder with methanol.

6.7.4.1.2 Add HCl dropwise (0.5—1.0 mL) while swirling, until the copper brightens.

6.7.4.1.3 Pour off the methanol/HCl and rinse 3 times with reagent water to remove all traces of acid, then 3 times with acetone, then 3 times with hexane.

6.7.4.1.4 For copper foil, cover with hexane after the final rinse. Store in a stoppered flask under nitrogen until used. For the powder, dry on a rotary evaporator. Store in a stoppered flask under nitrogen until used.

6.7.4.2 Tetrabutylammonium sulfite (TBA sulfite)

6.7.4.2.1 Tetrabutylammonium hydrogen sulfate, $[CH_3(CH_2)_3]_4NHSO_4$

6.7.4.2.2 Sodium sulfite, Na_2SO_3

6.7.4.2.3 Dissolve approximately 3 g tetrabutylammonium hydrogen sulfate in 100 mL of reagent water in an amber bottle with fluoropolymer-lined screw cap. Extract with three 20-mL portions of hexane and discard the hexane extracts.

6.7.4.2.4 Add 25 g sodium sulfite to produce a saturated solution. Store at room temperature. Replace after 1 month.

6.8 Standard solutions—Purchase as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepare from materials of known purity and composition. If compound purity is 96% or greater, the weight may be used without correction to compute the concentration of the standard. Store neat standards or single analyte standards in the dark at −20 to −10 °C in screw-cap vials with fluoropolymer-lined caps. Store multi-analyte standards at 4 °C or per manufacturer's recommendations. Place a mark on the vial at the level of the solution so that solvent evaporation loss can be detected. Bring the vial to room temperature prior to use to re-dissolve any precipitate.

6.8.1 Stock standard solutions—Standard solutions may be prepared from pure standard materials or purchased as certified solutions. Traceability must be to a national standard, when available. Except as noted below for solutions spiked into samples, prepare stock standards in isooctane or hexane. Observe the safety

precautions in Section 4. The following procedure may be used to prepare standards from neat materials.

6.8.1.1 Dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 10 mg of aldrin in a 10-mL ground-glass-stoppered volumetric flask and fill to the mark with isooctane or hexane. Larger volumes may be used at the convenience of the laboratory. After the aldrin is completely dissolved, transfer the solution to a 15-mL vial with fluoropolymer-lined cap.

6.8.1.2 Check for signs of degradation prior to preparation of calibration or performance-test standards.

6.8.1.3 Replace stock solutions after 12 months, or sooner if comparison with quality control check standards indicates a change in concentration.

6.8.2 Calibration solutions—It is necessary to prepare calibration solutions for the analytes of interest (Section 1.4) only using an appropriate solvent (isooctane or hexane may be used). Whatever solvent is used, both the calibration standards and the final sample extracts must use the same solvent. Other analytes may be included as desired.

6.8.2.1 Prepare calibration standards for the single-component analytes of interest and surrogates at a minimum of three concentration levels (five are suggested) by adding appropriate volumes of one or more stock standards to volumetric flasks. One of the calibration standards should be at a concentration of the analyte near the ML in Table 1 or 2. The ML value may be rounded to a whole number that is more convenient for preparing the standard, but must not exceed the ML values listed in Tables 1 or 2 for those analytes which list ML values. Alternatively, the laboratory may establish the ML for each analyte based on the concentration of the lowest calibration standard in a series of standards obtained from a commercial vendor, again, provided that the ML values does not exceed the MLs in Table 1 and 2, and provided that the resulting calibration meets the acceptance criteria in Section 7.5.2. based on the RSD, RSE, or R^2.

The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC system. A minimum of six concentration levels is required for a second order, non-linear (*e.g.,* quadratic; $ax^2 + bx + c$) calibration. Calibrations higher than second order are not allowed.

Given the number of analytes included in this method, it is highly likely that some will coelute on one or both of the GC columns used for the analysis. Therefore, divide the analytes two or more groups and prepare separate calibration standards for each group, at multiple concentrations (*e.g.,* a five-point calibration will require ten solutions to cover two groups of analytes).

Note: Many commercially available standards are divided into separate mixtures to address this issue.

The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC system. A separate standard near the MDL may be analyzed as a check on sensitivity, but should not be included in the linearity assessment. A minimum of six concentration levels is required for a non-linear (*e.g.,* quadratic) calibration (Section 7.5.2 or 7.6.2). The solvent for the standards must match the final solvent for the sample extracts (*e.g.,* isooctane or hexane).

Note: The option for non-linear calibration may be necessary to address specific instrumental techniques. However, it is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation or to avoid proper instrument maintenance.

6.8.2.2 Multi-component analytes (*e.g.,* PCBs as Aroclors, and Toxaphene)

6.8.2.2.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other Aroclor mixtures. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at three to five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing multi-point initial calibrations for each of the seven Aroclors. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample.

Therefore, prepare a minimum of three calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

6.8.2.2.2 Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards described in Section 6.8.2.2.1 have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors also may be used to determine the calibration factor for each Aroclor. Prepare a standard for each of the other Aroclors. The concentrations should generally correspond to the mid-point of the linear range of the detector, but lower concentrations may be employed at the discretion of the analyst based on project requirements.

6.8.2.2.3 For Toxaphene, prepare a minimum of three calibration standards containing Toxaphene by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

6.8.3 Quality Control (QC) Check Sample—Also known as the Laboratory Control Sample (LCS). Prepare a mid-level standard mixture in acetone (or water miscible solvent) from a stock solution from the same source as the calibration standards. This standard will be used to generate extracts to evaluate the capability of the laboratory.

6.8.4 Second Source Standard—Obtain standards from a second source (different manufacturer or different certified lot), and prepare a mid-level standard mixture in isooctane or hexane. This standard will be analyzed with the calibration curve to verify the accuracy of the calibration.

6.8.5 Internal standard solution—If the internal standard calibration technique is to be used, prepare pentachloronitrobenzene (PCNB) at a concentration of 10 µg/mL in ethyl acetate. Alternative and multiple internal standards; *e.g.*, tetrachloro-m-xylene, 4,4′-dibromobiphenyl, and/or decachlorobiphenyl may be used provided that the laboratory performs all QC tests and meets all QC acceptance criteria with the alternate or additional internal standard(s) as an integral part of this method.

6.8.6 Surrogate solution—Prepare a solution containing one or more surrogates at a concentration of 2 µg/mL in acetone. Potential surrogates include: Dibutyl chlorendate (DBC), tetrachloro-*m*-xylene (TCMX), 4,4′-dibromobiphenyl, or decachlorobiphenyl provided that the laboratory performs all QC tests and meets all QC acceptance criteria with the alternative surrogate(s) as an integral part of this method. If the internal standard calibration technique is used, do not use the internal standard as a surrogate.

6.8.7 DDT and endrin decomposition (breakdown) solution—Prepare a solution containing endrin at a concentration of 1 µg/mL and 4,4′-DDT at a concentration of 2 µg/mL, in isooctane or hexane.

6.8.8 Quality control check sample (laboratory control sample; LCS) concentrate—See Sections 8.2.1 and 8.4.

6.8.9 Stability of solutions—Analyze all standard solutions (Sections 6.8.1 through 6.8.8) within 48 hours of preparation. Replace purchased certified stock standard solutions per the expiration date. Replace stock standard solutions prepared by the laboratory or mixed with purchased solutions after one year, or sooner if comparison with QC check samples indicates a problem.

7. Calibration

7.1 Establish gas chromatographic operating conditions equivalent to those in Section 5.8.1 and Footnote 2 to Table 3. Alternative temperature program and flow rate conditions may be used. The system may be calibrated using the external standard technique (Section 7.5) or the internal standard technique (Section 7.6). It is necessary to calibrate the system for the analytes of interest (Section 1.4) only.

7.2 Separately inject the mid-level calibration standard for each calibration mixture. Store the retention time on each GC column.

7.3 Demonstrate that each column/detector system meets the MDLs in Table 3 or demonstrates sufficient sensitivity for the intended application and passes the DDT/endrin decomposition test (Section 13.5).

7.4 Injection of calibration solutions—Inject a constant volume in the range of 0.5 to 2.0 µL of each calibration solution into the GC column/detector pairs. Beginning with the lowest level mixture and proceeding to the highest level mixture may limit the risk of carryover from one standard to the next, but other sequences may be used. A blank sample should be analyzed after the highest standard to demonstrate that there is no carry-over within the system for this calibration range. For each analyte, compute, record, and store, as a function of the concentration injected, the retention time and peak area on each column/detector system. If multi-component analytes are to be analyzed, store the retention time and peak area for the three to five exclusive (unique large) peaks for each PCB or technical chlordane. Use four to six peaks for toxaphene.

7.5 External standard calibration

7.5.1 From the calibration data (Section 7.4), calculate the calibration factor (CF) for each analyte at each concentration according to the following equation:

$$CF = \frac{A_s}{C_s}$$

where:

C_s = Concentration of the analyte in the standard (ng/mL)

A_s = Peak height or area

For multi-component analytes, choose a series of characteristic peaks for each analyte (3 to 5 for each Aroclor, 4 to 6 for toxaphene) and calculate individual calibration factors for each peak. Alternatively, for toxaphene, sum the areas of all of the peaks in the standard chromatogram and use the summed area to determine the calibration factor. (If this alternative is used, the same approach must be used to quantitate the analyte in the samples.)

7.5.2 Calculate the mean (average) and relative standard deviation (RSD) of the calibration factors. If the RSD is less than 20%, linearity through the origin can be assumed and the average CF can be used for calculations. Alternatively, the results can be used to fit a linear or quadratic regression of response ratios, A_s/A_{is}, vs. concentration ratios C_s/C_{is}. If used, the regression must be weighted inversely proportional to concentration. The coefficient of determination (R^2) of the weighted regression must be greater than 0.99. Alternatively, the relative standard error (Reference 10) may be used as an acceptance criterion. As with the RSD, the RSE must be less than 20%. If an RSE less than 20% cannot be achieved for a quadratic regression, system performance is unacceptable and the system must be adjusted and re-calibrated.

Note: Regression calculations are not included in this method because the calculations are cumbersome and because many GC/ECD data systems allow selection of weighted regression for calibration and calculation of analyte concentrations.

7.6 Internal standard calibration

7.6.1 From the calibration data (Section 7.4), calculate the response factor (RF) for each analyte at each concentration according to the following equation:

$$RF = \frac{(A_s \text{ x } C_{is})}{(A_{is} \text{ x } C_s)}$$

where:

A_s = Response for the analyte to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard (ng/mL)

C_s = Concentration of the analyte to be measured (ng/mL).

7.6.2 Calculate the mean (average) and relative standard deviation (RSD) of the response factors. If the RSD is less than 15%, linearity through the origin can be assumed and the average RF can be used for calculations. Alternatively, the results can be used to prepare a calibration curve of response ratios, A_s/A_{is}, vs. concentration ratios, C_s/C_{is}, for the analyte. A minimum of six concentration levels is required for a non-linear (*e.g.*, quadratic) regression. If used, the regression must be weighted inversely proportional to concentration, and the correlation coefficient of the weighted regression must be greater than 0.99. The relative standard error (Reference 11) may also be used as an acceptance criterion. As with the RSD, the RSE must be less than 15%. If an RSE less than 15% cannot be achieved for a quadratic regression, system performance is unacceptable and the system must be adjusted and re-calibrated.

7.7 Second source standard—After the calibration curves are analyzed, analyze a second source standard at the mid-level concentration. This standard confirms the accuracy of the calibration curve. The concentrations must be within 20% difference of the true value. If the observed concentration exceeds this criteria, a third source may be analyzed to determine which standard was not accurate, and subsequent corrective actions taken.

7.8 The working calibration curve, CF, or RF must be verified at the beginning and end of each 24-hour shift by the analysis of a mid-level calibration standard or the combined QC standard (Section 6.8.2.1.3). Requirements for calibration verification are given in Section 13.6 and Table 4. Alternatively, calibration verification may be performed after a set number of injections (*e.g.*, every 20 injections), to include injection of extracts of field samples, QC samples, instrument blanks, etc. (*i.e.*, it is based on the number of injections performed, not sample extracts).

Note: The 24-hour shift begins after analysis of the combined QC standard (calibration verification) and ends 24 hours later. The ending calibration verification standard is run immediately after the last sample run during the 24-hour shift, so the beginning and ending calibration verifications are outside of the 24-hour shift. If calibration verification is based on the number of injections instead of time, then the ending verification standard for one group of 20 injections may be used as the beginning

verification for the next group of 20 injections.

7.9 Florisil® calibration—The column cleanup procedure in Section 11.3 utilizes Florisil column chromatography. Florisil® from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil® which is used, use of the lauric acid value (Reference 11) is suggested. The referenced procedure determines the adsorption from a hexane solution of lauric acid (mg) per g of Florisil®. The amount of Florisil® to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g. If cartridges containing Florisil® are used, then this step is not necessary.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and ongoing analysis of spiked samples and blanks to evaluate and document data quality. The laboratory must maintain records to document the quality of data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet performance requirements of this method. A quality control check standard (LCS, Section 8.4) must be prepared and analyzed with each batch of samples to confirm that the measurements were performed in an in-control mode of operation. A laboratory may develop its own performance criteria (as QC acceptance criteria), provided such criteria are as or more restrictive than the criteria in this method.

8.1.1 The laboratory must make an initial demonstration of the capability (IDC) to generate acceptable precision and recovery with this method. This demonstration is detailed in Section 8.2. On a continuing basis, the laboratory should repeat demonstration of capability (DOC) annually.

8.1.2 In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory is permitted certain options (Section 1.8 and 40 CFR 136.6(b) [Reference 12]) to improve separations or lower the costs of measurements. These options may include alternative extraction (*e.g.*, other solid-phase extraction materials and formats), concentration, and cleanup procedures, and changes in GC columns (Reference 12). Alternative determinative techniques, such as the substitution of spectroscopic or immunoassay techniques, and changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in this method is used, that technique must have a specificity equal to or greater than the specificity of the techniques in this method for the analytes of interest. The laboratory is also encouraged to participate in performance evaluation studies (see Section 8.8).

8.1.2.1 Each time a modification listed above is made to this method, the laboratory is required to repeat the procedure in Section 8.2. If the detection limit of the method will be affected by the change, the laboratory is required to demonstrate that the MDLs (40 CFR part 136, appendix B) are lower than one-third the regulatory compliance limit or as low as the MDLs in this method, whichever are greater. If calibration will be affected by the change, the instrument must be recalibrated per Section 7. Once the modification is demonstrated to produce results equivalent or superior to results produced by this method as written, that modification may be used routinely thereafter, so long as the other requirements in this method are met (*e.g.*, matrix spike/matrix spike duplicate recovery and relative percent difference).

8.1.2.1.1 If an allowed method modification, is to be applied to a specific discharge, the laboratory must prepare and analyze matrix spike/matrix spike duplicate (MS/MSD) samples (Section 8.3) and LCS samples (Section 8.4). The laboratory must include surrogates (Section 8.7) in each of the samples. The MS/MSD and LCS samples must be fortified with the analytes of interest (Section 1.4). If the modification is for nationwide use, MS/MSD samples must be prepared from a minimum of nine different discharges (See Section 8.1.2.1.2), and all QC acceptance criteria in this method must be met. This evaluation only needs to be performed once other than for the routine QC required by this method (for example it could be performed by the vendor of an alternate material) but any laboratory using that specific material must have the results of the study available. This includes a full data package with the raw data that will allow an independent reviewer to verify each determination and calculation performed by the laboratory (see Section 8.1.2.2.5, items a–q).

8.1.2.1.2 Sample matrices on which MS/MSD tests must be performed for nationwide use of an allowed modification:

(a) Effluent from a POTW

(b) ASTM D5905 Standard Specification for Substitute Wastewater

(c) Sewage sludge, if sewage sludge will be in the permit

(d) ASTM D1141 Standard Specification for Substitute Ocean Water, if ocean water will be in the permit

(e) Untreated and treated wastewaters up to a total of nine matrix types (see *http://water.epa.gov/scitech/wastetech/guide/industry.cfm*) for a list of industrial categories with existing effluent guidelines).

At least one of the above wastewater matrix types must have at least one of the following characteristics:

(i) Total suspended solids greater than 40 mg/L

(ii) Total dissolved solids greater than 100 mg/L

(iii) Oil and grease greater than 20 mg/L

(iv) NaCl greater than 120 mg/L

(v) $CaCO_3$ greater than 140 mg/L

The interim acceptance criteria for MS, MSD recoveries that do not have recovery limits specified in Table 5, and recoveries for surrogates that do not have recovery limits specified in Table 8, must be no wider than 60–140%, and the relative percent difference (RPD) of the concentrations in the MS and MSD that do not have RPD limits specified in Table 5 must be less than 30%. Alternatively, the laboratory may use the laboratory's in-house limits if they are tighter.

(f) A proficiency testing (PT) sample from a recognized provider, in addition to tests of the nine matrices (Section 8.1.2.1.1).

8.1.2.2 The laboratory must maintain records of modifications made to this method. These records include the following, at a minimum:

8.1.2.2.1 The names, titles, street addresses, telephone numbers, and email addresses of the analyst(s) that performed the analyses and modification, and of the quality control officer that witnessed and will verify the analyses and modifications.

8.1.2.2.2 A list of analytes, by name and CAS Registry number.

8.1.2.2.3 A narrative stating reason(s) for the modifications.

8.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

(a) Calibration (Section 7).

(b) Calibration verification (Section 13.6).

(c) Initial demonstration of capability (Section 8.2).

(d) Analysis of blanks (Section 8.5).

(e) Matrix spike/matrix spike duplicate analysis (Section 8.3).

(f) Laboratory control sample analysis (Section 8.4).

8.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

(a) Sample numbers and other identifiers.

(b) Extraction dates.

(c) Analysis dates and times.

(d) Analysis sequence/run chronology.

(e) Sample weight or volume (Section 10).

(f) Extract volume prior to each cleanup step (Sections 10 and 11).

(g) Extract volume after each cleanup step (Section 11).

(h) Final extract volume prior to injection (Sections 10 and 12).

(i) Injection volume (Sections 12.3 and 13.2).

(j) Sample or extract dilution (Section 15.4).

(k) Instrument and operating conditions.

(l) Column (dimensions, material, etc).

(m) Operating conditions (temperatures, flow rates, etc).

(n) Detector (type, operating conditions, etc).

(o) Chromatograms and other recordings of raw data.

(p) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.

(q) A written Standard Operating Procedure (SOP)

8.1.2.2.6 Each individual laboratory wishing to use a given modification must perform the start-up tests in Section 8.1.2 (*e.g.,* DOC, MDL), with the modification as an integral part of this method prior to applying the modification to specific discharges. Results of the DOC must meet the QC acceptance criteria in Table 5 for the analytes of interest (Section 1.4), and the MDLs must be equal to or lower than the MDLs in Table 3 for the analytes of interest.

8.1.3 Before analyzing samples, the laboratory must analyze a blank to demonstrate that interferences from the analytical system, lab ware, and reagents, are under control. Each time a batch of samples is extracted or reagents are changed, a blank must be extracted and analyzed as a safeguard against laboratory contamination. Requirements for the blank are given in Section 8.5.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 5% of all samples in a batch (Section 22.2) or from a given site or discharge, in duplicate, to monitor and evaluate method and laboratory performance on the sample matrix. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through analysis of a quality control check sample (laboratory control sample, LCS; on-going precision and recovery sample, OPR) that the measurement system is in control. This procedure is described in Section 8.4.

8.1.6 The laboratory should maintain performance records to document the quality of data that is generated. This procedure is given in Section 8.7.

8.1.7 The large number of analytes tested in performance tests in this method present a substantial probability that one or more will fail acceptance criteria when all analytes are tested simultaneously, and a re-test (reanalysis) is allowed if this situation should occur. If, however, continued re-testing results in further repeated failures, the laboratory should document the failures and either avoid reporting results for the analytes that failed or report the problem and failures with the data. A QC failure does not relieve a discharger or permittee of reporting timely results.

8.2 Demonstration of capability (DOC)—To establish the ability to generate acceptable recovery and precision, the laboratory must perform the DOC in Sections 8.2.1 through 8.2.6 for the analytes of interest initially and in an on-going manner at least annually. The laboratory must also establish MDLs for the analytes of interest using the MDL procedure at 40 CFR part 136, appendix B. The laboratory's MDLs must be equal to or lower than those listed in Table 3 or lower than one-third the regulatory compliance limit, whichever is greater. For MDLs not listed in Tables 1 or 2, the laboratory must determine the MDLs using the MDL procedure at 40 CFR part 136, appendix B under the same conditions used to determine the MDLs for the analytes listed in Tables 1 and 2. All procedures used in the analysis, including cleanup procedures, must be included in the DOC.

8.2.1 For the DOC, a QC check sample concentrate containing each analyte of interest (Section 1.4) is prepared in a water-miscible solvent using the solution in Section 6.8.3. The QC check sample concentrate must be prepared independently from those used for calibration, but should be from the same source and prepared in a water-miscible solvent. The concentrate should produce concentrations of the analytes of interest in water at or below the mid-point of the calibration range. Multiple solutions may be required.

Note: QC check sample concentrates are no longer available from EPA.

8.2.2 Using a pipet or syringe, prepare four QC check samples by adding an appropriate volume of the concentrate and of the surrogate(s) to each of four 1–L aliquots of reagent water. Swirl or stir to mix.

8.2.3 Extract and analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average percent recovery ($\bar{X}$) and the standard deviation (s) of the percent recovery for each analyte using the four results.

8.2.5 For each analyte, compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and recovery in Table 4. For analytes in Table 2 that are not listed in Table 4, QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 12 and 13). If s and $\bar{X}$ for all analytes of interest meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples can begin. If any individuals exceeds the precision limit or any individual $\bar{X}$ falls outside the range for recovery, system performance is unacceptable for that analyte.

Note: The large number of analytes in Tables 1 and 2 present a substantial probability that one or more will fail at least one of the acceptance criteria when many or all analytes are determined simultaneously.

8.2.6 When one or more of the analytes tested fail at least one of the acceptance criteria, repeat the test for only the analytes that failed. If results for these analytes pass, system performance is acceptable and analysis of samples and blanks may proceed. If one or more of the analytes again fail, system performance is unacceptable for the analytes that failed the acceptance criteria. Correct the problem and repeat the test (Section 8.2). See Section 8.1.7 for disposition of repeated failures.

Note: To maintain the validity of the test and re-test, system maintenance and/or adjustment is not permitted between this pair of tests.

8.3 Matrix spike and matrix spike duplicate (MS/MSD)—The laboratory must, on an ongoing basis, spike at least 5% of the samples in duplicate from each sample site being monitored to assess accuracy (recovery and precision). The data user should identify the sample and the analytes of interest (Section 1.4) to be spiked. If direction cannot be obtained, the laboratory must spike at least one

sample in duplicate per extraction batch of up to 20 samples (Section 22.2) with the analytes in Table 1. Spiked sample results should be reported only to the data user whose sample was spiked, or as requested or required by a regulatory/control authority.

8.3.1. If, as in compliance monitoring, the concentration of a specific analyte will be checked against a regulatory concentration limit, the concentration of the spike should be at that limit; otherwise, the concentration of the spike should be one to five times higher than the background concentration determined in Section 8.3.2, at or near the midpoint of the calibration range, or at the concentration in the LCS (Section 8.4) whichever concentration would be larger. When no information is available, the mid-point of the calibration may be used, as long as it is the same or less than the regulatory limit.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of the each analyte of interest. If necessary to meet the requirement in Section 8.3.1, prepare a new check sample concentrate (Section 8.2.1) appropriate for the background concentration. Spike and analyze two additional sample aliquots of the same volume as the original sample, and determine the concentrations after spiking (A_1 and A_2) of each analyte. Calculate the percent recoveries (P_1 and P_2) as:

$$P_x = \frac{A_x - B}{T} \times 100$$

where T is the known true value of the spike.

Also calculate the relative percent difference (RPD) between the concentrations (A_1 and A_2):

$$RPD = \frac{|A_1 - A_2|}{\frac{A_1 + A_2}{2}} \times 100$$

8.3.3 Compare the percent recoveries (P_1 and P_2) and the RPD for each analyte in the MS/MSD aliquots with the corresponding QC acceptance criteria for recovery (P) and RPD in Table 4.

If any individual P falls outside the designated range for recovery in either aliquot, or the RPD limit is exceeded, the result for the analyte in the unspiked sample is suspect and may not be reported or used for permitting or regulatory compliance. See Section 8.1.7 for disposition of failures.

For analytes in Table 2 not listed in Table 5, QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 12 and 13).

8.3.4 After analysis of a minimum of 20 MS/MSD samples for each target analyte and surrogate, the laboratory must calculate and apply in-house QC limits for recovery and RPD of future MS/MSD samples (Section 8.3). The QC limits for recovery are calculated as the mean observed recovery ±3 standard deviations, and the upper QC limit for RPD is calculated as the mean RPD plus 3 standard deviations of the RPDs. The in-house QC limits must be updated at least every two years and re-established after any major change in the analytical instrumentation or process. At least 80% of the analytes tested in the MS/MSD must have in-house QC acceptance criteria that are tighter than those in Table 4. If an in-house QC limit for the RPD is greater than the limit in Table 4, then the limit in Table 4 must be used. Similarly, if an in-house lower limit for recovery is below the lower limit in Table 4, then the lower limit in Table 4 must be used, and if an in-house upper limit for recovery is above the upper limit in Table 4, then the upper limit in Table 4 must be used. The laboratory must evaluate surrogate recovery data in each sample against its in-house surrogate recovery limits. The laboratory may use 60–140% as interim acceptance criteria for surrogate recoveries until in-house limits are developed.

8.4 Laboratory control sample (LCS)—A QC check sample (laboratory control sample, LCS; on-going precision and recovery sample, OPR) containing each single-component analyte of interest (Section 1.4) must be extracted, concentrated, and analyzed with each extraction batch of up to 20 samples (Section 3.1) to demonstrate acceptable recovery of the analytes of interest from a clean sample matrix. If multi-peak analytes are required, extract and prepare at least one as an LCS for each batch. Alternatively, the laboratory may set up a program where multi-peak LCS is rotated with a single-peak LCS.

8.4.1 Prepare the LCS by adding QC check sample concentrate (Section 8.2.1) to reagent water. Include all analytes of interest (Section 1.4) in the LCS. The volume of reagent water must be the same as the nominal volume used for the sample, the DOC (Section 8.2), the blank (Section 8.5), and the MS/MSD (Section 8.3). Also add a volume of the surrogate solution (Section 6.8.6).

8.4.2 Analyze the LCS prior to analysis of samples in the extraction batch (Section 3.1). Determine the concentration (A) of each analyte. Calculate the percent recovery as:

$$P_s = \frac{A}{T} \times 100$$

where T is the true value of the concentration in the LCS.

8.4.3 For each analyte, compare the percent recovery (P) with its corresponding QC acceptance criterion in Table 4. For analytes of interest in Table 2 not listed in Table 4, use the QC acceptance criteria developed for the MS/MSD (Section 8.3.3.2). If the recoveries for all analytes of interest fall within the designated ranges, analysis of blanks and field samples may proceed. If any individual recovery falls outside the range, proceed according to Section 8.4.4.

Note: The large number of analytes in Tables 1 and 2 present a substantial probability that one or more will fail the acceptance criteria when all analytes are tested simultaneously. Because a re-test is allowed in event of failure (Sections 8.1.7 and 8.4.4), it may be prudent to extract and analyze two LCSs together and evaluate results of the second analysis against the QC acceptance criteria only if an analyte fails the first test.

8.4.4 Repeat the test only for those analytes that failed to meet the acceptance criteria (P). If these analytes now pass, system performance is acceptable and analysis of blanks and samples may proceed. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, repeat the test using a fresh LCS (Section 8.2.1) or an LCS prepared with a fresh QC check sample concentrate (Section 8.2.1), or perform and document system repair. Subsequent to repair, repeat the LCS test (Section 8.4). See Section 8.1.7 for disposition of repeated failures.

8.4.5 After analysis of 20 LCS samples, the laboratory must calculate and apply in-house QC limits for recovery to future LCS samples (Section 8.4). Limits for recovery in the LCS are calculated as the mean recovery ±3 standard deviations. A minimum of 80% of the analytes tested for in the LCS must have QC acceptance criteria tighter than those in Table 4. As noted in Section 8.6, each laboratory must develop QC acceptance criteria for the surrogates they employ. The laboratory should use 60–140% as interim acceptance criteria for recoveries of spiked analytes and surrogates until in-house LCS and surrogate limits are developed. If an in-house lower limit for LCS recovery is lower than the lower limit in Table 4, the lower limit in Table 4 must be used, and if an in-house upper limit for recovery is higher than the upper limit in Table 4, the upper limit in Table 4 must be used.

8.5 Blank—Extract and analyze a blank with each extraction batch (Section 22.2) to demonstrate that the reagents and equipment used for preparation and analysis are free from contamination.

8.5.1 Prepare the blank from reagent water and spike it with the surrogates. The volume of reagent water must be the same as the volume used for samples, the DOC (Section 8.2), the LCS (Section 8.4), and the MS/MSD (Section 8.3). Extract, concentrate, and analyze the blank using the same procedures and reagents used for the samples, LCS, and MS/MSD in the batch. Analyze the blank immediately after analysis of the LCS (Section 8.4) and prior to analysis of the MS/MSD and samples to demonstrate freedom from contamination.

8.5.2 If any analyte of interest is found in the blank at a concentration greater than the MDL for the analyte, at a concentration greater than one-third the regulatory compliance limit, or at a concentration greater than one-tenth the concentration in a sample in the batch (Section 3.1), whichever is greatest, analysis of samples must be halted and samples in the batch must be re-extracted and the extracts reanalyzed. Samples in a batch must be associated with an uncontaminated blank before the results for those samples may be reported or used for permitting or regulatory compliance purposes. If re-testing of blanks results in repeated failures, the laboratory should document the failures and report the problem and failures with the data.

8.6 Surrogate recovery—As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solution (Section 6.8.6) per Section 10.2.2 or 10.4.2, analyze the samples, and calculate the percent recovery of each surrogate. QC acceptance criteria for surrogates must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 12 and 13). If any recovery fails its criterion, attempt to find and correct the cause of the failure, and if sufficient volume is available, re-extract another aliquot of the affected sample. Surrogate recoveries from the blank and LCS may be used as pass/fail criteria by the laboratory or as required by a regulatory authority, or may be used to diagnose problems with the analytical system.

8.7 As part of the QC program for the laboratory, it is suggested but not required that method accuracy for wastewater samples be assessed and records maintained. After analysis of five or more spiked wastewater samples as in Section 8.4, calculate the average percent recovery ($\bar{X}$) and the standard deviation of the percent recovery (sp). Express the accuracy assessment as a percent interval from $\bar{X} - 2sp$ to $\bar{X} + 2sp$. For example, if $\bar{X} = 90\%$ and sp = 10%, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each analyte on a regular basis to ensure process control (*e.g.,* after each 5–10 new accuracy measurements).

8.8 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with another dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Collect samples as grab samples in glass bottles, or in refrigerated bottles using automatic sampling equipment. Collect 1–L of ambient waters, effluents, and other aqueous samples. If high concentrations of the analytes of interest are expected (*e.g.,* for untreated effluents or in-process waters), collect a smaller volume (*e.g.,* 250 mL), but not less than 100 mL, in addition to the 1–L sample. Follow conventional sampling practices, except do not pre-rinse the bottle with sample before collection. Automatic sampling equipment must be as free as possible of polyvinyl chloride or other tubing or other potential sources of contamination. If needed, collect additional sample(s) for the MS/MSD (Section 8.3).

9.2 Ice or refrigerate the sample at <6 °C from the time of collection until extraction, but do not freeze. If aldrin is to be determined and residual chlorine is present, add 80 mg/L of sodium thiosulfate but do not add excess. Any method suitable for field use may be employed to test for residual chlorine (Reference 14). If sodium thiosulfate interferes in the determination of the analytes, an alternative preservative (*e.g.,* ascorbic acid or sodium sulfite) may be used.

9.3 Extract all samples within seven days of collection and completely analyze within 40 days of extraction (Reference 1). If the sample will not be extracted within 72 hours of collection, adjust the sample pH to range of 5.0–9.0 with sodium hydroxide solution or sulfuric acid. Record the volume of acid or base used.

10. Sample Extraction

10.1 This section contains procedures for separatory funnel liquid-liquid extraction (SFLLE, Section 10.2), continuous liquid-liquid extraction (CLLE, Section 10.4), and disk-based solid-phase extraction (SPE, Section 10.5). SFLLE is faster, but may not be as effective as CLLE for extracting polar analytes. SFLLE is labor intensive and may result in formation of emulsions that are difficult to break. CLLE is less labor intensive, avoids emulsion formation, but requires more time (18–24 hours), more hood space, and may require more solvent. SPE can be faster, unless the particulate load in an aqueous sample is so high that it slows the filtration process. If an alternative extraction scheme to those detailed in this method is used, all QC tests must be performed and all QC acceptance criteria must be met with that extraction scheme as an integral part of this method.

10.2 Separatory funnel liquid-liquid extraction (SFLLE).

10.2.1 The SFLLE procedure below assumes a sample volume of 1 L. When a different sample volume is extracted, adjust the volume of methylene chloride accordingly.

10.2.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into the separatory funnel. Pipet the surrogate standard spiking solution (Section 6.8.6) into the separatory funnel. If the sample will be used for the LCS or MS or MSD, pipet the appropriate QC check sample concentrate (Section 8.2.1) into the separatory funnel. Mix well. If the sample arrives in a larger sample bottle, 1 L may be measured in a graduated cylinder, then added to the separatory funnel.

Note: Instances in which the sample is collected in an oversized bottle should be reported by the laboratory to the data user. Of particular concern is that fact that this practice precludes rinsing the empty bottle with solvent as described below, which could leave hydrophobic pesticides on the wall of the bottle, and underestimate the actual sample concentrations.

10.2.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two

minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If an emulsion forms and the emulsion interface between the layers is more than one-third the volume of the solvent layer, employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, freezing, or other physical methods. Collect the methylene chloride extract in a flask. If the emulsion cannot be broken (recovery of less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Section 10.4.

10.2.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the flask. Perform a third extraction in the same manner. Proceed to macro-concentration (Section 10.3.1).

10.2.5 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to an appropriately sized graduated cylinder. Record the sample volume to the nearest 5 mL. Sample volumes may also be determined by weighing the container before and after extraction or filling to the mark with water.

10.3 Concentration.

10.3.1 Macro concentration.

10.3.1.1 Assemble a Kuderna-Danish (K–D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K–D concentrator so long as the requirements of Section 8.2 are met.

10.3.1.2 Pour the extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K–D concentrator. Rinse the flask and column with 20–30 mL of methylene chloride to complete the quantitative transfer.

10.3.1.3 If no cleanup is to be performed on the sample, add 500 µL (0.5 mL) of isooctane to the extract to act as a keeper during concentration.

10.3.1.4 Add one or two clean boiling chips and attach a three-ball Snyder column to the K–D evaporative flask. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. At the proper rate of evaporation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL or other determined amount, remove the K–D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

10.3.1.5 If the extract is to be cleaned up by a procedure for sulfur removal, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. Adjust the final volume to 10 mL in methylene chloride and proceed to sulfur removal (Section 11.5). If the extract is to cleaned up using one of the other cleanup procedures or is to be injected into the GC, proceed to Kuderna-Danish micro-concentration (Section 10.3.2) or nitrogen evaporation and solvent exchange (Section 10.3.3).

10.3.2 Kuderna-Danish micro concentration.

10.3.2.1 Add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro-Snyder column. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65 °C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5–10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches approximately 1 mL or other required amount, remove the K–D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of methylene chloride, and proceed to Section 10.3.3 for nitrogen evaporation and solvent exchange.

10.3.3 Nitrogen evaporation and solvent exchange—Extracts to be subjected to solid-phase cleanup (SPE) are exchanged into 1.0 mL of the SPE elution solvent (Section 6.7.2.2). Extracts to be subjected to Florisil® or alumina cleanups are exchanged into hexane. Extracts that have been cleaned up and are ready for analysis are exchanged into isooctane or hexane, to match the solvent used for the calibration standards.

10.3.3.1 Transfer the vial containing the sample extract to the nitrogen evaporation (blowdown) device (Section 5.2.5.2). Lower the vial into a 50–55 °C water bath and begin concentrating. During the solvent evaporation process, do not allow the extract to become dry. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed. A large vortex in the solvent may cause analyte loss.

10.3.3.2 Solvent exchange.

10.3.3.2.1 When the volume of the liquid is approximately 500 µL, add 2 to 3 mL of the desired solvent (SPE elution solvent for SPE cleanup, hexane for Florisil or alumina, or isooctane for final injection into the GC) and continue concentrating to approximately 500 µL. Repeat the addition of solvent and concentrate once more.

10.3.3.3.2 Adjust the volume of an extract to be cleaned up by SPE, Florisil®, or alumina to 1.0 mL. Proceed to extract cleanup (Section 11).

10.3.3.3 Extracts that have been cleaned up and are ready for analysis—Adjust the final extract volume to be consistent with the volume extracted and the sensitivity desired. The goal is for a full-volume sample (*e.g.,* 1–L) to have a final extract volume of 10 mL, but other volumes may be used.

10.3.4 Transfer the concentrated extract to a vial with fluoropolymer-lined cap. Seal the vial and label with the sample number. Store in the dark at room temperature until ready for GC analysis. If GC analysis will not be performed on the same day, store the vial in the dark at 4 °C. Analyze the extract by GC per the procedure in Section 12.

10.4 Continuous liquid/liquid extraction (CLLE).

10.4.1 Use CLLE when experience with a sample from a given source indicates an emulsion problem, or when an emulsion is encountered using SFLLE. CLLE may be used for all samples, if desired.

10.4.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Transfer the sample to the continuous extractor and, using a pipet, add surrogate standard spiking solution. If the sample will be used for the LCS, MS, or MSD, pipet the appropriate check sample concentrate (Section 8.2.1 or 8.3.2) into the separatory funnel. Mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor.

10.4.3 Repeat the sample bottle rinse with two additional 50–100 mL portions

of methylene chloride and add the rinses to the extractor.

10.4.4 Add a suitable volume of methylene chloride to the distilling flask (generally 200–500 mL) and sufficient reagent water to ensure proper operation of the extractor, and extract the sample for 18–24 hours. A shorter or longer extraction time may be used if all QC acceptance criteria are met. Test and, if necessary, adjust the pH of the water during the second or third hour of the extraction. After extraction, allow the apparatus to cool, then detach the distilling flask. Dry, concentrate, solvent exchange, and transfer the extract to a vial with fluoropolymer-lined cap, per Section 10.3.

10.4.5 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to an appropriately sized graduated cylinder. Record the sample volume to the nearest 5 mL. Sample volumes may also be determined by weighing the container before and after extraction or filling to the mark with water.

10.5 Solid-phase extraction of aqueous samples.

The steps in this section address the extraction of aqueous field samples using disk-based solid-phase extraction (SPE) media, based on an ATP approved by EPA in 1995 (Reference 20). This application of SPE is distinct from that used in this method for the cleanup of sample extracts in Section 11.2. Analysts must be careful not to confuse the equipment, supplies, or the procedural steps from these two different uses of SPE.

Note: Changes to the extraction conditions described below may be made by the laboratory under the allowance for method flexibility described in Section 8.1, provided that the performance requirements in Section 8.2 are met. However, changes in SPE materials, formats, and solvents must meet the requirements in Section 8.1.2 and its subsections.

10.5.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. If the sample contains particulates, let stand to settle out the particulates before extraction.

10.5.2 Extract the sample as follows:

10.5.2.1 Place a 90-mm standard filter apparatus on a vacuum filtration flask or manifold and attach to a vacuum source. The vacuum gauge should read at least 25 in. of mercury when all valves are closed. Position a 90-mm C18 extraction disk onto the filter screen. Wet the entire disk with methanol. To aid in filtering samples with particulates, a 1-µm glass fiber filter or Empore® Filter Aid 400 can be placed on the top of the disk and wetted with methanol. Install the reservoir and clamp. Resume vacuum to dry the disk. Interrupt the vacuum. Wash the disk and reservoir with 20 mL of methylene chloride. Resume the vacuum briefly to pull methylene chloride through the disk. Interrupt the vacuum and allow the disk to soak for about a minute. Resume vacuum and completely dry the disk.

10.5.2.2 Condition the disk with 20 mL of methanol. Apply vacuum until nearly all the solvent has passed through the disk, interrupting it while solvent remains on the disk. Allow the disk to soak for about a minute. Resume vacuum to pull most of the methanol through, but interrupting it to leave a layer of methanol on the surface of the disk. Do not allow disk to dry.

For uniform flow and good recovery, it is critical the disk not be allowed to dry from now until the end of the extraction. Discard waste solvent. Rinse the disk with 20 mL of deionized water. Resume vacuum to pull most of the water through, but interrupt it to leave a layer of water on the surface of the disk. Do not allow the disk to dry. If disk does dry, recondition with methanol as above.

10.5.2.3 Add the water sample to the reservoir and immediately apply the vacuum. If particulates have settled in the sample, gently decant the clear layer into the apparatus until most of the sample has been processed. Then pour the remainder including the particulates into the reservoir. Empty the sample bottle completely. When the filtration is complete, dry the disk for three minutes. Turn off the vacuum.

10.5.3 Discard sample filtrate. Insert tube to collect the eluant. The tube should fit around the drip tip of the base. Reassemble the apparatus. Add 5.0 mL of acetone to the center of the disk, allowing it to spread evenly over the disk. Turn the vacuum on and quickly off when the filter surface nears dryness but still remains wet. Allow to soak for 15 seconds. Add 20 mL of methylene chloride to the sample bottle, seal and shake to rinse the inside of the bottle. Transfer the methylene chloride from the bottle to the filter. Resume the vacuum slowly so as to avoid splashing.

Interrupt the vacuum when the filter surface nears dryness but still remains wet. Allow disk to soak in solvent for 20 seconds. Rinse the reservoir glass and disk with 10 mL of methylene chloride. Resume vacuum slowly. Interrupt vacuum when disk is covered with solvent. Allow to soak for 20 seconds. Resume vacuum to dry the disk. Remove the sample tube.

10.5.4 Dry, concentrate, solvent exchange, and transfer the extract to a vial with fluoropolymer-lined cap, per Section 10.3.

10.5.5 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to an appropriately sized graduated cylinder. Record the sample volume to the nearest 5 mL. Sample volumes may also be determined by weighing the container before and after extraction or filling to the mark with water.

11. Extract Cleanup

11.1 Cleanup may not be necessary for a relatively clean sample matrix. If particular circumstances require the use of a cleanup procedure, the laboratory may use any or all of the procedures below or any other appropriate procedure (*e.g.,* gel permeation chromatography). However, the laboratory must first repeat the tests in Sections 8.2, 8.3, and 8.4 to demonstrate that the requirements of those sections can be met using the cleanup procedure(s) as an integral part of this method. This is particularly important when the target analytes for the analysis include any of the single component pesticides in Table 2, because some cleanups have not been optimized for all of those analytes.

11.1.1 The solid-phase cartridge (Section 11.2) removes polar organic compounds such as phenols.

11.1.2 The Florisil® column (Section 11.3) allows for selected fractionation of the organochlorine analytes and will also eliminate polar interferences.

11.1.3 Alumina column cleanup (Section 11.4) also removes polar materials.

11.1.4 Elemental sulfur, which interferes with the electron capture gas chromatography of some of the pesticides, may be removed using activated copper, or TBA sulfite. Sulfur removal (Section 11.5) is required when sulfur is known or suspected to be present. Some chlorinated pesticides which also contain sulfur may be removed by this cleanup.

11.2 Solid-phase extraction (SPE) as a cleanup.

In order to use the C18 SPE cartridge in Section 5.5.3.5 as a cleanup procedure, the sample extract must be exchanged from methylene chloride to methylene chloride: acetonitrile:hexane. Follow the solvent exchange steps in Section 10.3.3.2 prior to attempting solid-phase cleanup.

Note: This application of SPE is distinct from that used in this method for the extraction of aqueous samples in Section 10.5. Analysts must be careful not to confuse the equipment, supplies, or procedural steps from these two different uses of SPE.

11.2.1 Setup.

11.2.1.1 Attach the VacElute Manifold (Section 5.5.3.2) to a water aspirator or vacuum pump with the trap and gauge installed between the manifold and vacuum source.

11.2.1.2 Place the SPE cartridges in the manifold, turn on the vacuum source, and adjust the vacuum to 5 to 10 psi.

11.2.2 Cartridge washing—Pre-elute each cartridge prior to use sequentially with 10-mL portions each of hexane, methanol, and water using vacuum for 30 seconds after each eluting solvent. Follow this pre-elution with 1 mL methylene chloride and three 10-mL portions of the elution solvent (Section 6.7.2.2) using vacuum for 5 minutes after each eluting solvent. Tap the cartridge lightly while under vacuum to dry between solvent rinses. The three portions of elution solvent may be collected and used as a cartridge blank, if desired. Finally, elute the cartridge with 10 mL each of methanol and water, using the vacuum for 30 seconds after each eluant.

11.2.3 Extract cleanup.

11.2.3.1 After cartridge washing (Section 11.2.2), release the vacuum and place the rack containing the 50-mL volumetric flasks (Section 5.5.3.4) in the vacuum manifold. Re-establish the vacuum at 5 to 10 psi.

11.2.3.2 Using a pipette or a 1-mL syringe, transfer 1.0 mL of extract to the SPE cartridge. Apply vacuum for five minutes to dry the cartridge. Tap gently to aid in drying.

11.2.3.3 Elute each cartridge into its volumetric flask sequentially with three 10-mL portions of the methylene chloride:acetonitrile:hexane (50:3:47) elution solvent (Section 6.7.2.2), using vacuum for five minutes after each portion. Collect the eluants in the 50-mL volumetric flasks.

11.2.3.4 Release the vacuum and remove the 50-mL volumetric flasks.

11.2.3.5 Concentrate the eluted extracts per Section 10.3.

11.3 Florisil®.

In order to use Florisil cleanup, the sample extract must be exchanged from methylene chloride to hexane. Follow the solvent exchange steps in Section 10.3.3.2 prior to attempting Florisil® cleanup.

Note: Alternative formats for this cleanup may be used by the laboratory, including cartridges containing Florisil®. If an alternative format is used, consult the manufacturer's instructions and develop a formal documented procedure to replace the steps in Section 11.3 of this method and demonstrate that the alternative meets the relevant quality control requirements of this method.

11.3.1 If the chromatographic column does not contain a frit at the bottom, place a small plug of pre-cleaned glass wool in the column (Section 5.2.4) to retain the Florisil®. Place the mass of Florisil® (nominally 20 g) predetermined by calibration (Section 7.9 and Table 6) in a chromatographic column. Tap the column to settle the Florisil® and add 1 to 2 cm of granular anhydrous sodium sulfate to the top.

11.3.2 Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil®. Just prior to exposure of the sodium sulfate layer to the air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluant.

11.3.3 Transfer the concentrated extract (Section 10.3.3) onto the column. Complete the transfer with two 1-mL hexane rinses, drawing the extract and rinses down to the level of the sodium sulfate.

11.3.4 Place a clean 500-mL K–D flask and concentrator tube under the column. Elute Fraction 1 with 200 mL of 6% (v/v) ethyl ether in hexane at a rate of approximately 5 mL/min. Remove the K–D flask and set it aside for later concentration. Elute Fraction 2 with 200 mL of 15% (v/v) ethyl ether in hexane into a second K–D flask. Elute Fraction 3 with 200 mL of 50% (v/v) ethyl ether in hexane into a third K–D flask. The elution patterns for the pesticides and PCBs are shown in Table 6.

11.3.5 Concentrate the fractions as in Section 10.3, except use hexane to prewet the column and set the water bath at about 85 °C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the volume of Fraction 1 to approximately 10 mL for sulfur removal (Section 11.5), if required; otherwise, adjust the volume of the fractions to 10 mL, 1.0 mL, or other volume needed for the sensitivity desired. Analyze the concentrated extract by gas chromatography (Section 12).

11.4 Alumina.

The sample extract must be exchanged from methylene chloride to hexane. Follow the solvent exchange steps in Section 10.3.3.2 prior to attempting alumina cleanup.

11.4.1 If the chromatographic column does not contain a frit at the bottom, place a small plug of pre-cleaned glass wool in the chromatographic column (Section 5.2.4) to retain the alumina. Add 10 g of alumina (Section 6.7.3) on top of the plug. Tap the column to settle the alumina. Place 1–2 g of anhydrous sodium sulfate on top of the alumina.

11.4.2 Close the stopcock and fill the column to just above the sodium sulfate with hexane. Add 25 mL of hexane. Open the stopcock and adjust the flow rate of hexane to approximately 2 mL/min. Do not allow the column to go dry throughout the elutions.

11.4.3 When the level of the hexane is at the top of the column, quantitatively transfer the extract to the column. When the level of the extract is at the top of the column, slowly add 25 mL of hexane and elute the column to the level of the sodium sulfate. Discard the hexane.

11.4.4 Place a K–D flask (Section 5.2.5.1.2) under the column and elute the pesticides with approximately 150 mL of hexane:ethyl ether (80:20 v/v). It may be necessary to adjust the volume of elution solvent for slightly different alumina activities.

11.4.5 Concentrate the extract per Section 10.3.

11.5 Sulfur removal—Elemental sulfur will usually elute in Fraction 1 of the Florisil® column cleanup. If Florisil® cleanup is not used, or to remove sulfur from any of the Florisil® fractions, use one of the sulfur removal procedures below. These procedures may be applied to extracts in hexane, ethyl ether, or methylene chloride.

Note: Separate procedures using copper or TBA sulfite are provided in this section for sulfur removal. They may be used separately or in combination, if desired.

11.5.1 Removal with copper (Reference 15).

Note: Some of the analytes in Table 2 are not amenable to sulfur removal with copper (*e.g.,* atrazine and diazinon). Therefore, before using copper to remove sulfur from an extract that will be analyzed for any of the non-PCB analytes in Table 2, the laboratory must demonstrate that the analytes can be extracted from an aqueous sample matrix that contains sulfur and recovered from an extract treated with copper. Acceptable performance can be demonstrated through the preparation and analysis of a matrix spike sample that meets the QC requirements for recovery.

11.5.1.1 Quantitatively transfer the extract to a 40- to 50-mL flask or bottle. If there is evidence of water in the K–D or round-bottom flask after the transfer, rinse the flask with small portions of hexane:acetone (40:60) and add to the flask or bottle. Mark and set aside the concentration flask for future use.

11.5.1.2 Add 10–20 g of granular anhydrous sodium sulfate to the flask. Swirl to dry the extract.

11.5.1.3 Add activated copper (Section 6.7.4.1.4) and allow to stand for 30–60 minutes, swirling occasionally. If

the copper does not remain bright, add more and swirl occasionally for another 30–60 minutes.

11.5.1.4 After drying and sulfur removal, quantitatively transfer the extract to a nitrogen-evaporation vial or tube and proceed to Section 10.3.3 for nitrogen evaporation and solvent exchange, taking care to leave the sodium sulfate and copper foil in the flask.

11.5.2 Removal with TBA sulfite.

11.5.2.1 Using small volumes of hexane, quantitatively transfer the extract to a 40- to 50-mL centrifuge tube with fluoropolymer-lined screw cap.

11.5.2.2 Add 1–2 mL of TBA sulfite reagent (Section 6.7.4.2.4), 2–3 mL of 2-propanol, and approximately 0.7 g of sodium sulfite (Section 6.7.4.2.2) crystals to the tube. Cap and shake for 1–2 minutes. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 0.5-g portions until a solid residue remains after repeated shaking.

11.5.2.3 Add 5–10 mL of reagent water and shake for 1–2 minutes. Centrifuge to settle the solids.

11.5.2.4 Quantitatively transfer the hexane (top) layer through a small funnel containing a few grams of granular anhydrous sodium sulfate to a nitrogen-evaporation vial or tube and proceed to Section 10.3.3 for micro-concentration and solvent exchange.

12. Gas Chromatography

12.1 Establish the same operating conditions used in Section 7.1 for instrument calibration.

12.2 If the internal standard calibration procedure is used, add the internal standard solution (Section 6.9.3) to the extract as close as possible to the time of injection to minimize the possibility of loss by evaporation, adsorption, or reaction. For example, add 1 µL of 10 µg/mL internal standard solution into the extract, assuming no dilutions. Mix thoroughly.

12.3 Simultaneously inject an appropriate volume of the sample extract or standard solution onto both columns, using split, splitless, solvent purge, large-volume, or on-column injection. Alternatively, if using a single-column GC configuration, inject an appropriate volume of the sample extract or standard solution onto each GC column independently. If the sample is injected manually, the solvent-flush technique should be used. The injection volume depends upon the technique used and the sensitivity needed to meet MDLs or reporting limits for regulatory compliance. Injected volumes must be the same for all standards and sample extracts. Record the volume injected to the nearest 0.05 µL.

12.4 Set the data system or GC control to start the temperature program upon sample injection, and begin data collection after the solvent peak elutes. Set the data system to stop data collection after the last analyte is expected to elute and to return the column to the initial temperature.

12.5 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When standards and extracts are not being used for analyses, store them refrigerated at <6 °C, protected from light, in screw-cap vials equipped with un-pierced fluoropolymer-lined septa.

13. System and Laboratory Performance

13.1 At the beginning of each shift during which standards or extracts are analyzed, GC system performance and calibration must be verified for all analytes and surrogates on both column/detector systems. Adjustment and/or recalibration (per Section 7) are performed until all performance criteria are met. Only after all performance criteria are met may samples, blanks and other QC samples, and standards be analyzed.

13.2 Inject an aliquot of the combined QC standard (Section 6.8.4) on both columns. Inject an aliquot of each of the multi-component standards.

13.3 Retention times—The absolute retention times of the peak maxima shall be within ±2 seconds of the retention times in the calibration verification (Section 7.8).

13.4 GC resolution—Resolution is acceptable if the valley height between two peaks (as measured from the baseline) is less than 40% of the shorter of the two peaks.

13.4.1 DB–608 column—DDT and endrin aldehyde.

13.4.2 DB–1701 column—alpha and gamma chlordane.

Note: If using other GC columns or stationary phases, these resolution criteria apply to these four target analytes and any other closely eluting analytes on those other GC columns.

13.5 Decomposition of DDT and endrin—If DDT, endrin, or their breakdown products are to be determined, this test must be performed prior to calibration verification (Section 13.6). DDT decomposes to DDE and DDD. Endrin decomposes to endrin aldehyde and endrin ketone.

13.5.1 Inject 1 µL of the DDT and endrin decomposition solution (Section 6.9.5).

13.5.2 Measure the areas of the peaks for DDT, DDE, DDD, Endrin, Endrin aldehyde, and Endrin ketone in the chromatogram and calculate the percent breakdown as shown in the equations below:

$$\%\ \text{breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDD + DDE)}}{\text{sum of all peak areas (DDT + DDE + DDD)}} \times 100$$

$$\%\ \text{breakdown of Endrin} = \frac{\text{sum of degradation peak areas (Endrin aldehyde + Endrin ketone)}}{\text{sum of all peak areas (Endrin + Endrin aldehyde + Endrin ketone)}} \times 100$$

13.5.3 Both the % breakdown of DDT and of Endrin must be less than 20%, otherwise the system is not performing acceptably for DDT and endrin. In this case, repair the GC column system that failed and repeat the performance tests (Sections 13.2 to 13.6) until the specification is met.

Note: DDT and endrin decomposition are usually caused by accumulations of particulates in the injector and in the front end of the column. Cleaning and silanizing the injection port liner, and breaking off a short section of the front end of the column will usually eliminate the decomposition problem. Either of these corrective actions may affect retention times, GC resolution, and calibration linearity.

13.6 Calibration verification.

13.6.1 Compute the percent recovery of each analyte and of the coeluting analytes, based on the initial calibration data (Section 7.5 or 7.6).

13.6.2 For each analyte or for coeluting analytes, compare the concentration with the limits for calibration verification in Table 4. For coeluting analytes, use the coeluting analyte with the least restrictive

specification (the widest range). For analytes in Table 2 not listed in Table 4, QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 13 and 14). If the recoveries for all analytes meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may continue. If, however, any recovery falls outside the calibration verification range, system performance is unacceptable for that analyte. If this occurs, repair the system and repeat the test (Section 13.6), or prepare a fresh calibration standard and repeat the test, or recalibrate (Section 7). See Section 8.1.7 for information on repeated test failures.

13.7 Laboratory control sample.

13.7.1 Analyze the extract of the combined QC standard (a.k.a. LCS) (Section 6.8.3) extracted with each sample batch (Section 8.4).

13.7.2 Compute the percent recovery of each analyte and of the coeluting analytes.

13.7.3 For each analyte or coeluting analytes, compare the percent recovery with the limits for ''P'' in Table 4. For coeluting analytes, use the coeluting analyte with the least restrictive specification (widest range). If all analytes pass, the extraction, concentration, and cleanup processes are in control and analysis of blanks and samples may proceed. If, however, any of the analytes fail, these processes are not in control. In this event, correct the problem, re-extract the sample batch, and repeat the ongoing precision and recovery test.

13.7.4 It is suggested, but not required, that the laboratory update statements of data quality. Add results that pass the specifications in Section 13.7.3 to initial (Section 8.7) and previous ongoing data. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of percent recovery, sr. Express the accuracy as a recovery interval from R − 2sr to R + 2sr. For example, if R = 95% and sr = 5%, the accuracy is 85 to 105%.

13.8 Internal standard response—If internal standard calibration is used, verify that detector sensitivity has not changed by comparing the response (area or height) of each internal standard in the sample, blank, LCS, MS, and MSD to the response in the combined QC standard (Section 6.8.3). The peak area or height of the internal standard should be within 50% to 200% (½ to 2×) of its respective peak area or height in the verification standard. If the area or height is not within this range, compute the concentration of the analytes using the external standard method (Section 7.5).

14. Qualitative Identification

14.1 Identification is accomplished by comparison of data from analysis of a sample, blank, or other QC sample with data from calibration verification (Section 7.7.1 or 13.5), and with data stored in the retention-time and calibration libraries (Section 7.7). The retention time window is determined as described in Section 14.2. Identification is confirmed when retention time agrees on both GC columns, as described below.

14.2 Establishing retention time windows.

14.2.1 Using the data from the multi-point initial calibration (Section 7.4), determine the retention time in decimal minutes (not minutes:seconds) of each peak representing a single-component target analyte on each column/detector system. For the multi-component analytes, use the retention times of the five largest peaks in the chromatograms on each column/detector system.

14.2.2 Calculate the standard deviation of the retention times for each single-component analyte on each column/detector system and for the three to five exclusive (unique large) peaks for each multi-component analyte.

14.2.3 Define the width of the retention time window as three times that standard deviation. Establish the center of the retention time window for each analyte by using the absolute retention time for each analyte from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration. If the calculated RT window is less than 0.02 minutes, then use 0.02 minutes as the window.

Note: Procedures for establishing retention time windows from other sources may be employed provided that they are clearly documented and provide acceptable performance. Such performance may be evaluated using the results for the spiked QC samples described in this method, such as laboratory control samples and matrix spike samples.

14.2.4 New retention time windows must be established when a new GC column is installed or if a GC column has been shortened during maintenance to a degree that the retention times of analytes in the calibration verification standard have shifted close to the lower limits of the established retention time windows.

14.2.5 RT windows should be checked periodically by examining the peaks in spiked samples such as the LCS or MS/MSD to confirm that peaks for known analytes are properly identified.

14.2.6 If the retention time of an analyte in the initial calibration data has been evaluated as described in Section 7.4.1 and it varied by more than 5 seconds across the calibration range as a function of the concentration of the standard (see Section 7.4.2), then using the standard deviation of the retention times to set the width of the retention time window may not adequately serve to identify the analyte in question under routine conditions. In such cases, data from additional analyses of standards may be required to adequately model the chromatographic behavior of the analyte.

14.3 Identifying the analyte in a sample.

14.3.1 In order to identify a single-component analyte from analysis of a sample, blank, or other QC sample, the peak representing the analyst must fall within its respective retention time windows on both column/detector systems (as defined in Section 14.2). That identification is further supported by the comparison of the numerical results on both columns, as described in Section 15.7.

14.3.2 In order to identify a multi-component analyte, pattern matching (fingerprinting) may be used, or the three to five exclusive (unique, baseline resolved, and largest) peaks for that analyte must fall within their respective retention time windows on both column/detector systems (as defined in Section 14.2). That identification is further supported by the comparison of the numerical results on both columns, as described in Section 15.7.

14.4 GC/MS confirmation.

When the concentration of an analyte is sufficient, or if the presence or identity is suspect, its presence should be confirmed by GC/MS. In order to match the sensitivity of the GC/ECD, confirmation will have to be by SIM–GC/MS, or estimated the concentration would have to be 100 times higher than the GC/ECD calibration range.

14.5 Additional information that may aid the laboratory in the identification of an analyte.

The occurrence of peaks eluting near the retention time of an analyte of interest increases the probability of a false positive for the analyte. If the concentration is insufficient for confirmation by GC/MS, the laboratory may use the cleanup procedures in this

method (Section 11) on a new sample aliquot to attempt to remove the interferent. After attempts at cleanup are exhausted, the following steps may be helpful to assure that the substance that appears in the RT windows on both columns is the analyte of interest.

14.5.1 Determine the consistency of the RT data for the analyte on each column. For example, if the RT is very stable (*i.e.,* varies by no more than a few seconds) for the calibration, calibration verification, blank, LCS, and MS/MSD, the RT for the analyte of interest in the sample should be within this variation regardless of the window established in Section 14.2. If the analyte is not within this variation on both columns, it is likely not present.

14.5.2 The possibility exists that the RT for the analyte in a sample could shift if extraneous materials are present. This possibility may be able to be confirmed or refuted by the behavior of the surrogates in the sample. If multiple surrogates are used that span the length of the chromatographic run, the RTs for the surrogates on both columns are consistent with their RTs in calibration, calibration verification, blank, LCS, and MS/MSD, it is unlikely that the RT for the analyte of interest has shifted.

14.5.3 If the RT for the analyte is shifted slightly later on one column and earlier on the other, and the surrogates have not shifted, it is highly unlikely that the analyte is present, because shifts nearly always occur in the same direction on both columns.

15. Quantitative Determination

15.1 External standard quantitation—Calculate the concentration of the analyte in the extract using the calibration curve or average calibration factor determined in calibration (Section 7.5.2) and the following equation:

$$C_{ex} = \frac{A_s}{CF}$$

where:

C_{ex} = Concentration of the analyte in the extract (ng/mL)
A_s = Peak height or area for the analyte in the standard or sample
CF = Calibration factor, as defined in Section 7.5.1

15.2 Internal standard quantitation—Calculate the concentration of the analyte in the extract using the calibration curve or average response factor determined in calibration (Section 7.6.2) and the following equation:

$$C_{ex} = \frac{A_s \times C_{is}}{A_{is} \times RF}$$

where:

C_{ex} = Concentration of the analyte in the extract (ng/mL)
A_s = Peak height or area for the analyte in the standard or sample
C_{is} = Concentration of the internal standard (ng/mL)
A_{is} = Area of the internal standard
RF = Response factor, as defined in Section 7.6.1

15.3 Calculate the concentration of the analyte in the sample using the concentration in the extract, the extract volume, the sample volume, and the dilution factor, per the following equation:

$$C_s = \frac{C_{ex} \times V_{ex} \times DF}{V_s \times 1000}$$

where:

C_s = Concentration of the analyte in the sample (µg/L)
V_{ex} = Final extract volume (mL)
C_{ex} = Concentration in the extract (ng/mL)
V_s = Volume of sample (L)
DF = Dilution factor
and the factor of 1,000 in the denominator converts the final units from ng/L to µg/L

15.4 If the concentration of any target analyte exceeds the calibration range, either extract and analyze a smaller sample volume, or dilute and analyze the diluted extract.

15.5 Quantitation of multi-component analytes

15.5.1 PCBs as Aroclors

Quantify an Aroclor by comparing the sample chromatogram to that of the most similar Aroclor standard as indicated in Section 14.3.2. Compare the responses of 3 to 5 major peaks in the calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks chosen in Sec. 7.5.1. Determine the concentration of each of the characteristic peaks, using the average calibration factor calculated for that peak in Sec. 7.5.2, and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor.

15.5.2 Other multi-component analytes

Quantify any other multi-component analytes (technical chlordane or toxaphene) using the same peaks used to develop the average calibration factors in Section 7.5.2. Determine the concentration of each of the characteristic peaks, and then the concentrations represented by those characteristic peaks are averaged to determine the concentration of the analyte. Alternatively, for toxaphene, the analyst may determine the calibration factor in Section 7.5.2 by summing the areas of all of the peaks for the analyte and using the summed of the peak areas in the sample chromatogram to determine the concentration. However, the approach used for toxaphene must be the same for the calibration and the sample analyses.

15.6 Reporting of results.

As noted in Section 1.6.1, EPA has promulgated this method at 40 CFR part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described here are focused on such monitoring needs and may not be relevant to other uses of the method.

15.6.1 Report results for wastewater samples in µg/L without correction for recovery. (Other units may be used if required by in a permit.) Report all QC data with the sample results.

15.6.2 Reporting level.

Unless otherwise specified in by a regulatory authority or in a discharge permit, results for analytes that meet the identification criteria are reported down to the concentration of the ML established by the laboratory through calibration of the instrument (see Section 7.5 or 7.6 and the glossary for the derivation of the ML). EPA considers the terms ''reporting limit,'' ''quantitation limit,'' and ''minimum level'' to be synonymous.

15.6.2.1 Report the lower result from the two columns (see Section 15.7 below) for each analyte in each sample, blank, or standard at or above the ML to 3 significant figures. Report a result for each analyte found in each sample below the ML as ''ML,'' or as required by the regulatory authority or permit. Results are reported without blank subtraction unless requested or required by a regulatory authority or in a permit. In this case, both the sample result and the blank results must be reported together.

15.6.2.2 In addition to reporting results for samples and blank(s) separately, the concentration of each analyte in a blank or field blank associated with that sample may be subtracted from the result for that sample, but only if requested or required by a regulatory authority or in a permit. In this case, both the sample result and the blank results must be reported together.

15.6.2.3 Report the result for an analyte in a sample or extract that has been diluted at the least dilute level at which the peak area is within the calibration range (*i.e.,* above the ML for the analyte) and the MS/MSD recovery and RPD are within their respective QC acceptance criteria (Table 4). This may

require reporting results for some analytes from different analyses.

The results for each analyte in the MS/MSD samples should be reported from the same GC column as used to report the results for that analyte in the unspiked sample. If the MS/MSD recoveries and RPDs calculated in this manner do not meet the acceptance criteria in Table 4, then the analyst may use the results from the other GC column to determine if the MS/MSD results meet the acceptance criteria. If such a situation occurs, the results for the sample should be recalculated using the same GC column data as used for the MS/MSD samples, and reported with appropriate annotations that alert the data user of the issue.

15.6.2.4 Results from tests performed with an analytical system that is not in control (*i.e.,* that does not meet acceptance criteria for all of QC tests in this method) must not be reported or otherwise used for permitting or regulatory compliance purposes, but do not relieve a discharger or permittee of reporting timely results. If the holding time would be exceeded for a re-analysis of the sample, the regulatory/control authority should be consulted for disposition.

15.6.3 Analyze the sample by GC/MS or on a third column when analytes have co-eluted or interfere with determination on both columns.

Note: Dichlone and kepone do not elute from the DB–1701 column and must be confirmed on a DB–5 column, or by GC/MS.

15.7 Quantitative information that may aid in the confirmation of the presence of an analyte

15.7.1 As noted in Section 14.3, the relative agreement between the numerical results from the two GC columns may be used to support the identification of the target analyte by providing evidence that that co-eluting interferences are not present at the retention time of the target analyte. Calculate the percent difference (%D) between the results for the analyte from both columns, as follows:

$$\%D = \frac{\text{Higher result} - \text{Lower result}}{\text{Higher result}} \text{ x } 100$$

In general, if the %D of the two results is less than 50% (*e.g.,* a factor of 2), then the pesticide is present. This %D is generous and allows for the pesticide that has the largest measurement error.

Note: Laboratories may employ metrics less than 50% for this comparison, including those specified in other analytical methods for these pesticides (*e.g.,* CLP or SW–846).

15.7.2 If the amounts do not agree, and the RT data indicate the presence of the analyte (per Section 14), it is likely that a positive interference is present on the column that yielded the higher result. That interferent may be represented by a separate peak on the other column that does not coincide with the retention time of any of the target analytes. If the interfering peak is evident on the other column, report the result from that column and advise the data user that the interference resulted in a %D value greater than 50%.

If an interferent is not identifiable on the second column, then the results must be reported as ''not detected'' at the lower concentration. In this event, the pesticide is not confirmed and the reporting limit is elevated.

Note: The resulting elevation of the reporting limit may not meet the requirements for compliance monitoring and the use of additional cleanup procedures may be required.

16. Analysis of Complex Samples

16.1 Some samples may contain high levels (greater than 1 µg/L) of the analytes of interest, interfering analytes, and/or polymeric materials. Some samples may not concentrate to 1.0 mL (Section 10.3.3.3.2); others may overload the GC column and/or detector.

16.2 When an interference is known or suspected to be present, the laboratory should attempt to clean up the sample extract using the SPE cartridge (Section 11.2), by Florisil® (Section 11.3), Alumina (Section 11.4), sulfur removal (Section 11.5), or another clean up procedure appropriate to the analytes of interest. If these techniques do not remove the interference, the extract is diluted by a known factor and reanalyzed (Section 12). Dilution until the extract is lightly colored is preferable. Typical dilution factors are 2, 5, and 10.

16.3 Recovery of surrogate(s)—In most samples, surrogate recoveries will be similar to those from reagent water. If surrogate recovery is outside the range developed in Section 8.6, the sample is re-extracted and reanalyzed if there is sufficient sample and if it is within the 7-day extraction holding time. If the surrogate recovery is still outside this range, extract and analyze one-tenth the volume of sample to overcome any matrix interference problems. If a sample is highly colored or suspected to be high in concentration, a 1–L sample aliquot and a 100-mL sample aliquot could be extracted simultaneously and still meet the holding time criteria, while providing information about a complex matrix.

16.4 Recovery of the matrix spike and matrix spike duplicate (MS/MSD)—In most samples, MS/MSD recoveries will be similar to those from reagent water. If either the MS or MSD recovery is outside the range specified in Section 8.3.3, one-tenth the volume of sample is spiked and analyzed. If the matrix spike recovery is still outside the range, the result for the unspiked sample may not be reported or used for permitting or regulatory compliance purposes. Poor matrix spike recovery does not relieve a discharger or permittee of reporting timely results.

17. Method Performance

17.1 This method was tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 4x MDL to 1000x MDL with the following exceptions: Chlordane recovery at 4x MDL was low (60%); Toxaphene recovery was demonstrated linear over the range of 10x MDL to 1000x MDL (Reference 3).

17.2 The 1984 version of this method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations (Reference 2). Concentrations used in the study ranged from 0.5 to 30 µg/L for single-component pesticides and from 8.5 to 400 µg/L for multi-component analytes. These data are for a subset of analytes described in the current version of the method.

17.3 During the development of Method 1656, a similar EPA procedure for the organochlorine pesticides, single-operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 5.

18. Pollution Prevention

18.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operations. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, the laboratory should use pollution prevention techniques to address waste generation. When wastes cannot be reduced at the source, the Agency recommends recycling as the next best option.

18.2 The analytes in this method are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards. This method utilizes significant quantities of methylene chloride. Laboratories are encouraged to recover and recycle this and other solvents during extract concentration.

18.3 For information about pollution prevention that may be applied to laboratories and research institutions, consult Less is Better: Laboratory Chemical Management for Waste Reduction (Reference 19).

19. Waste Management

19.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. An overview of requirements can be found in Environmental Management Guide for Small Laboratories (EPA 233–B–98–001).

19.2 Samples at pH <2, or pH >12 are hazardous and must be neutralized before being poured down a drain, or must be handled as hazardous waste.

19.3 Many analytes in this method decompose above 500 °C. Low-level waste such as absorbent paper, tissues, animal remains, and plastic gloves may be burned in an appropriate incinerator. Gross quantities of neat or highly concentrated solutions of toxic or hazardous chemicals should be packaged securely and disposed of through commercial or governmental channels that are capable of handling toxic wastes.

20. References

1. ''Determination of Pesticides and PCBs in Industrial and Municipal Wastewaters,'' EPA 600/4–82–023, National Technical Information Service, PB82–214222, Springfield, Virginia 22161, April 1982.
2. ''EPA Method Study 18 Method 608-Organochlorine Pesticides and PCBs,'' EPA 600/4–84–061, National Technical Information Service, PB84–211358, Springfield, Virginia 22161, June 1984.
3. ''Method Detection Limit and Analytical Curve Studies, EPA Methods 606, 607, and 608,'' Special letter report for EPA Contract 68–03–2606, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, June 1980.
4. ASTM Annual Book of Standards, Part 31, D3694–78. ''Standard Practice for Preparation of Sample Containers and for Preservation of Organic Constituents,'' American Society for Testing and Materials, Philadelphia.
5. Giam, C.S., Chan, H.S., and Nef, G.S. ''Sensitive Method for Determination of Phthalate Ester Plasticizers in Open-Ocean Biota Samples,'' Analytical Chemistry, 47, 2225 (1975).
6. Giam, C.S. and Chan, H.S. ''Control of Blanks in the Analysis of Phthalates in Air and Ocean Biota Samples,'' U.S. National Bureau of Standards, Special Publication 442, pp. 701–708, 1976.
7. Solutions to Analytical Chemistry Problems with Clean Water Act Methods, EPA 821–R–07–002, March 2007.
8. ''Carcinogens-Working With Carcinogens,'' Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77–206, August 1977.
9. ''Occupational Exposure to Hazardous Chemicals in Laboratories,'' (29 CFR part 1910, subpart 1450), Occupational Safety and Health Administration, OSHA.
10. 40 CFR 136.6(b)(4)(j).
11. Mills, P.A. ''Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns,'' Journal of the Association of Official Analytical Chemists, 51, 29, (1968).
12. 40 CFR 136.6(b)(2)(i).
13. Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water (EPA–821–B–98–003) March 1999.
14. Methods 4500 Cl F and 4500 Cl G, Standard Methods for the Examination of Water and Wastewater, published jointly by the American Public Health Association, American Water Works Association, and Water Environment Federation, 1015 Fifteenth St. Washington, DC 20005, 20th Edition, 2000.
15. ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples,'' EPA–600/8–80–038, U.S. Environmental Protection Agency, Health Effects Research Laboratory, Research Triangle Park, North Carolina.
16. USEPA, 2000, Method 1656 Organo-Halide Pesticides In Wastewater, Soil, Sludge, Sediment, and Tissue by GC/HSD, EPA–821–R–00–017, September 2000.
17. USEPA, 2010, Method 1668C Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, EPA–820–R–10–005, April 2010.
18. USEPA, 2007, Method 1699: Pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, EPA–821–R–08–001, December 2007.
19. ''Less is Better,'' American Chemical Society on-line publication, *http://www.acs.org/content/dam/acsorg/about/governance/committees/chemicalsafety/publications/less-is-better.pdf.*
20. EPA Method 608 ATP 3M0222, An alternative test procedure for the measurement of organochlorine pesticides and polychlorinated biphenyls in waste water. **Federal Register**/Vol. 60, No. 148 August 2, 1995.

21. Tables

TABLE 1—PESTICIDES [1]

Analyte	CAS No.	MDL [2] (ng/L)	ML [3] (ng/L)
Aldrin	309–00–2	8	24
alpha-BHC	319–84–6	6	18
beta-BHC	319–85–7	7	21
delta-BHC	319–86–8	5	15
gamma-BHC (Lindane)	58–89–9	1	33
alpha-Chlordane	5103–71–9	9	27
gamma-Chlordane	5103–74–2	8	24
4,4′-DDD	72–54–8	5	15
4,4′-DDE	72–55–9	10	30
4,4′-DDT	50–29–3	12	36
Dieldrin	60–57–1	6	18
Endosulfan I	959–98–8	11	33
Endosulfan II	33213–65–9	8	24
Endosulfan sulfate	1031–07–8	7	21
Endrin	72–20–8	4	12
Endrin aldehyde	7421–93–4	11	33
Heptachlor	76–44–8	5	15
Heptachlor epoxide	1024–57–3	12	36

[1] All analytes in this table are Priority Pollutants (40 CFR part 423, appendix A).
[2] 40 CFR 136, Appendix B. MDLs were obtained by a single laboratory with an electrolytic conductivity detector, and are estimates of what can be achieved using an electron capture detector.
[3] ML = Minimum Level—see Glossary for definition and derivation.

TABLE 2—ADDITIONAL ANALYTES

Analyte	CAS No.	MDL [3] (ng/L)	ML [4] (ng/L)
Acephate	30560–19–1	2,000	6,000
Alachlor	15972–60–8	20	60
Atrazine	1912–24–9	500	1,500
Benfluralin (Benefin)	1861–40–1	20	60
Bromacil	314–40–9	70	210
Bromoxynil octanoate	1689–99–2	30	90
Butachlor	23184–66–9	30	90
Captafol	2425–06–1	100	300
Captan	133–06–2	100	300
Carbophenothion (Trithion)	786–19–6	50	150
Chlorobenzilate	510–15–6	25	75
Chloroneb (Terraneb)	2675–77–6		
Chloropropylate (Acaralate)	5836–10–2		
Chlorothalonil	1897–45–6	15	45
Cyanazine	21725–46–2		
DCPA (Dacthal)	1861–32–1	3	9
2,4′-DDD	53–19–0		
2,4′-DDE	3424–82–6		
2,4′-DDT	789–02–6		
Diallate (Avadex)	2303–16–4	45	135
1,2-Dibromo-3-chloropropane (DBCP)	96–12–8		
Dichlone	117–80–6		
Dichloran	99–30–9		
Dicofol	115–32–2		
Endrin ketone	53494–70–5	8	24
Ethalfluralin (Sonalan)	55283–68–6	5	15
Etridiazole	2593–15–9		
Fenarimol (Rubigan)	60168–88–9	20	30
Hexachlorobenzene [1]	118–74–1		
Hexachlorocyclopentadiene [1]	77–47–4		
Isodrin	465–73–6	13	39
Isopropalin (Paarlan)	33820–53–0	20	60
Kepone	143–50–0	100	300
Methoxychlor	72–43–5	30	90
Metolachlor	51218–45–2		
Metribuzin	21087–64–9	5	15
Mirex	2385–85–5	4	12
Nitrofen (TOK)	1836–75–5	13	39
cis-Nonachlor	5103–73–1		
trans-Nonachlor	39765–80–5		
Norfluorazon	27314–13–2	50	150

TABLE 2—ADDITIONAL ANALYTES—Continued

Analyte	CAS No.	MDL [3] (ng/L)	ML [4] (ng/L)
Octachlorostyrene	29082–74–4		
Oxychlordane	27304–13–8		
PCNB (Pentachloronitrobenzene)	82–68–8	6	18
Pendamethalin (Prowl)	40487–42–1		
cis-Permethrin	61949–76–6	200	600
trans-Permethrin	61949–77–7	200	600
Perthane (Ethylan)	72–56–0		
Propachlor	1918–16–7		
Propanil	709–98–8		
Propazine	139–40–2		
Quintozene	82–68–8		
Simazine	122–34–9	400	1,200
Strobane	8001–50–1		
Technazene	117–18–0		
Technical Chlordane [2]			
Terbacil	5902–51–2	200	600
Terbuthylazine	5915–41–3	300	900
Toxaphene [1]	8001–35–2	910	2,730
Trifluralin	1582–09–8	50	150
PCB–1016 [1]	12674–11–2	150	450
PCB–1221 [1]	11104–28–2	150	450
PCB–1232 [1]	11141–16–5	150	450
PCB–1242 [1]	53469–21–9	150	450
PCB–1248 [1]	12672–29–6	150	450
PCB–1254 [1]	11097–69–1	150	450
PCB–1260 [1]	11096–82–5	140	420

[1] Priority Pollutants (40 CFR part 423, appendix A).
[2] Technical Chlordane may be used in cases where historical reporting has only been for this form of Chlordane.
[3] 40 CFR part 136, appendix B. MDLs were obtained by a single laboratory with an electrolytic conductivity detector, and are estimates of what can be achieved using an electron capture detector.
[4] ML = Minimum Level—see Glossary for definition and derivation.

TABLE 3—EXAMPLE RETENTION TIMES [1]

Analyte	Retention time (min) [2]	
	DB-608	DB-1701
Acephate	5.03	([3])
Trifluralin	5.16	6.79
Ethalfluralin	5.28	6.49
Benfluralin	5.53	6.87
Diallate-A	7.15	6.23
Diallate-B	7.42	6.77
alpha-BHC	8.14	7.44
PCNB	9.03	7.58
Simazine	9.06	9.29
Atrazine	9.12	9.12
Terbuthylazine	9.17	9.46
gamma-BHC (Lindane)	9.52	9.91
beta-BHC	9.86	11.90
Heptachlor	10.66	10.55
Chlorothalonil	10.66	10.96
Dichlone	10.80	([4])
Terbacil	11.11	12.63
delta-BHC	11.20	12.98
Alachlor	11.57	11.06
Propanil	11.60	14.10
Aldrin	11.84	11.46
DCPA	12.18	12.09
Metribuzin	12.80	11.68
Triadimefon	12.99	13.57
Isopropalin	13.06	13.37
Isodrin	13.47	11.12
Heptachlor epoxide	13.97	12.56
Pendamethalin	14.21	13.46
Bromacil	14.39	([3])

TABLE 3—EXAMPLE RETENTION TIMES [1]—Continued

Analyte	Retention time (min) [2]	
	DB-608	DB-1701
alpha-Chlordane	14.63	14.20
Butachlor	15.03	15.69
gamma-Chlordane	15.24	14.36
Endosulfan I	15.25	13.87
4,4′-DDE	16.34	14.84
Dieldrin	16.41	15.25
Captan	16.83	15.43
Chlorobenzilate	17.58	17.28
Endrin	17.80	15.86
Nitrofen (TOK)	17.86	17.47
Kepone	17.92	([3 5])
4,4′-DDD	18.43	17.77
Endosulfan II	18.45	18.57
Bromoxynil octanoate	18.85	18.57
4,4′-DDT	19.48	18.32
Carbophenothion	19.65	18.21
Endrin aldehyde	19.72	19.18
Endosulfan sulfate	20.21	20.37
Captafol	22.51	21.22
Norfluorazon	20.68	22.01
Mirex	22.75	19.79
Methoxychlor	22.80	20.68
Endrin ketone	23.00	21.79
Fenarimol	24.53	23.79
cis-Permethrin	25.00	23.59
trans-Permethrin	25.62	23.92
PCB-1242.		
PCB-1232.		
PCB-1016.		
PCB-1221.		

TABLE 3—EXAMPLE RETENTION TIMES [1]—Continued

Analyte	Retention time (min) [2]	
	DB-608	DB-1701
PCB-1248.		
PCB-1254.		
PCB-1260 (5 peaks)	15.44	14.64
	15.73	15.36
	16.94	16.53
	17.28	18.70
	19.17	19.92
Toxaphene (5 peaks)	16.60	16.60
	17.37	17.52
	18.11	17.92
	19.46	18.73
	19.69	19.00

[1] Data from EPA Method 1656 (Reference 16).
[2] Columns: 30-m long × 0.53-mm ID fused-silica capillary; DB-608, 0.83 μm; and DB-1701, 1.0 μm.
Conditions suggested to meet retention times shown: 150 °C for 0.5 minute, 150–270 °C at 5 °C/min, and 270 °C until *trans*-Permethrin elutes.
Carrier gas flow rates approximately 7 mL/min.
[3] Does not elute from DB-1701 column at level tested.
[4] Not recovered from water at the levels tested.
[5] Dichlone and Kepone do not elute from the DB-1701 column and should be confirmed on DB-5.

TABLE 4—QC ACCEPTANCE CRITERIA

Analyte	Calibration verification (%)	Test concentration (µg/L)	Limit for s (% SD)	Range for $\overline{X}$ (%)	Range for P (%)	Maximum MS/MSD RPD (%)
Aldrin	75–125	2.0	25	54–130	42–140	35
alpha-BHC	69–125	2.0	28	49–130	37–140	36
beta-BHC	75–125	2.0	38	39–130	17–147	44
delta-BHC	75–125	2.0	43	51–130	19–140	52
gamma-BHC	75–125	2.0	29	43–130	32–140	39
alpha-Chlordane	73–125	50.0	24	55–130	45–140	35
gamma-Chlordane	75–125	50.0	24	55–130	45–140	35
4,4′-DDD	75–125	10.0	32	48–130	31–141	39
4,4′-DDE	75–125	2.0	30	54–130	30–145	35
4,4′-DDT	75–125	10.0	39	46–137	25–160	42
Dieldrin	48–125	2.0	42	58–130	36–146	49
Endosulfan I	75–125	2.0	25	57–141	45–153	28
Endosulfan II	75–125	10.0	63	22–171	D–202	53
Endosulfan sulfate	70–125	10.0	32	38–132	26–144	38
Endrin	5–125	10.0	42	51–130	30–147	48
Heptachlor	75–125	2.0	28	43–130	34–140	43
Heptachlor epoxide	75–125	2.0	22	57–132	37–142	26
Toxaphene	68–134	50.0	30	56–130	41–140	41
PCB-1016	75–125	50.0	24	61–103	50–140	36
PCB-1221	75–125	50.0	50	44–150	15–178	48
PCB-1232	75–125	50.0	32	28–197	10–215	25
PCB-1242	75–125	50.0	26	50–139	39–150	29
PCB-1248	75–125	50.0	32	58–140	38–158	35
PCB-1254	75–125	50.0	34	44–130	29–140	45
PCB-1260	75–125	50.0	28	37–130	8–140	38

S = Standard deviation of four recovery measurements (Section 8.2.4).

Note: These criteria were developed from data in Table 5 (Reference 2). Where necessary, limits for recovery have been broadened to assure applicability to concentrations below those in Table 5.

TABLE 5—PRECISION AND RECOVERY AS FUNCTIONS OF CONCENTRATION

Analyte	Recovery, X′ (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S′ (µg/L)
Aldrin	0.81C + 0.04	0.16($\overline{X}$) − 0.04	0.20($\overline{X}$) − 0.01
alpha-BHC	0.84C + 0.03	0.13($\overline{X}$) + 0.04	0.23($\overline{X}$) − 0.00
beta-BHC	0.81C + 0.07	0.22($\overline{X}$) − 0.02	0.33($\overline{X}$) − 0.05
delta-BHC	0.81C + 0.07	0.18($\overline{X}$) + 0.09	0.25($\overline{X}$) + 0.03
gamma-BHC (Lindane)	0.82C − 0.05	0.12($\overline{X}$) + 0.06	0.22($\overline{X}$) + 0.04
Chlordane	0.82C − 0.04	0.13 ($\overline{X}$) + 0.13	0.18($\overline{X}$) + 0.18
4,4′-DDD	0.84C + 0.30	0.20($\overline{X}$) − 0.18	0.27($\overline{X}$) − 0.14
4,4′-DDE	0.85C + 0.14	0.13($\overline{X}$) + 0.06	0.28($\overline{X}$) − 0.09
4,4′-DDT	0.93C − 0.13	0.17($\overline{X}$) + 0.39	0.31($\overline{X}$) − 0.21
Dieldrin	0.90C + 0.02	0.12($\overline{X}$) + 0.19	0.16($\overline{X}$) + 0.16
Endosulfan I	0.97C + 0.04	0.10($\overline{X}$) + 0.07	0.18($\overline{X}$) + 0.08
Endosulfan II	0.93C + 0.34	0.41($\overline{X}$) − 0.65	0.47($\overline{X}$) − 0.20
Endosulfan sulfate	0.89C − 0.37	0.13($\overline{X}$) + 0.33	0.24($\overline{X}$) + 0.35
Endrin	0.89C − 0.04	0.20($\overline{X}$) + 0.25	0.24($\overline{X}$) + 0.25
Heptachlor	0.69C + 0.04	0.06($\overline{X}$) + 0.13	0.16($\overline{X}$) + 0.08
Heptachlor epoxide	0.89C + 0.10	0.18($\overline{X}$) − 0.11	0.25($\overline{X}$) − 0.08
Toxaphene	0.80C + 1.74	0.09($\overline{X}$) + 3.20	0.20($\overline{X}$) + 0.22
PCB-1016	0.81C + 0.50	0.13($\overline{X}$) + 0.15	0.15($\overline{X}$) + 0.45
PCB-1221	0.96C + 0.65	0.29($\overline{X}$) − 0.76	0.35($\overline{X}$) − 0.62
PCB-1232	0.91C + 10.8	0.21($\overline{X}$) − 1.93	0.31($\overline{X}$) + 3.50
PCB-1242	0.93C + 0.70	0.11($\overline{X}$) + 1.40	0.21($\overline{X}$) + 1.52
PCB-1248	0.97C + 1.06	0.17($\overline{X}$) + 0.41	0.25($\overline{X}$) − 0.37
PCB-1254	0.76C + 2.07	0.15($\overline{X}$) + 1.66	0.17($\overline{X}$) + 3.62
PCB-1260	0.66C + 3.76	0.22($\overline{X}$) − 2.37	0.39($\overline{X}$) − 4.86

X′ = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

TABLE 6—DISTRIBUTION OF CHLORINATED PESTICIDES AND PCBS INTO FLORISIL® COLUMN FRACTIONS

Analyte	Percent recovery by fraction [1]		
	1	2	3
Aldrin	100		
alpha-BHC	100		
beta-BHC	97		
delta-BHC	98		
gamma-BHC (Lindane)	100		
Chlordane	100		
4,4′-DDD	99		
4,4′-DDE	.....	98	
4,4′-DDT	100		
Dieldrin	0	100	

TABLE 6—DISTRIBUTION OF CHLORINATED PESTICIDES AND PCBS INTO FLORISIL® COLUMN FRACTIONS—Continued

Analyte	Percent recovery by fraction [1]		
	1	2	3
Endosulfan I	37	64	.....
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Heptachlor	100		
Heptachlor epoxide	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		

TABLE 6—DISTRIBUTION OF CHLORINATED PESTICIDES AND PCBS INTO FLORISIL® COLUMN FRACTIONS—Continued

Analyte	Percent recovery by fraction [1]		
	1	2	3
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260.			

[1] Eluant composition:
Fraction 1—6% ethyl ether in hexane
Fraction 2—15% ethyl ether in hexane
Fraction 3—50% ethyl ether in hexane.

BILLING CODE 6560–50–P

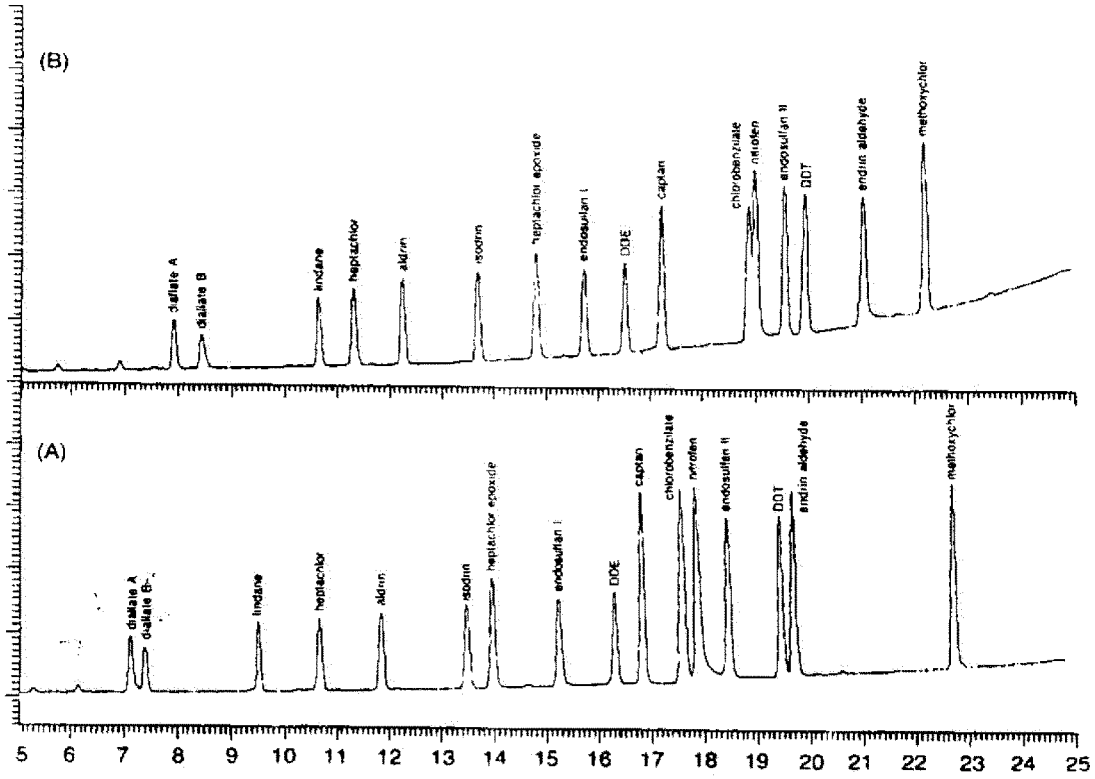


Figure 1 Example Chromatogram of Selected Organochlorine Pesticides

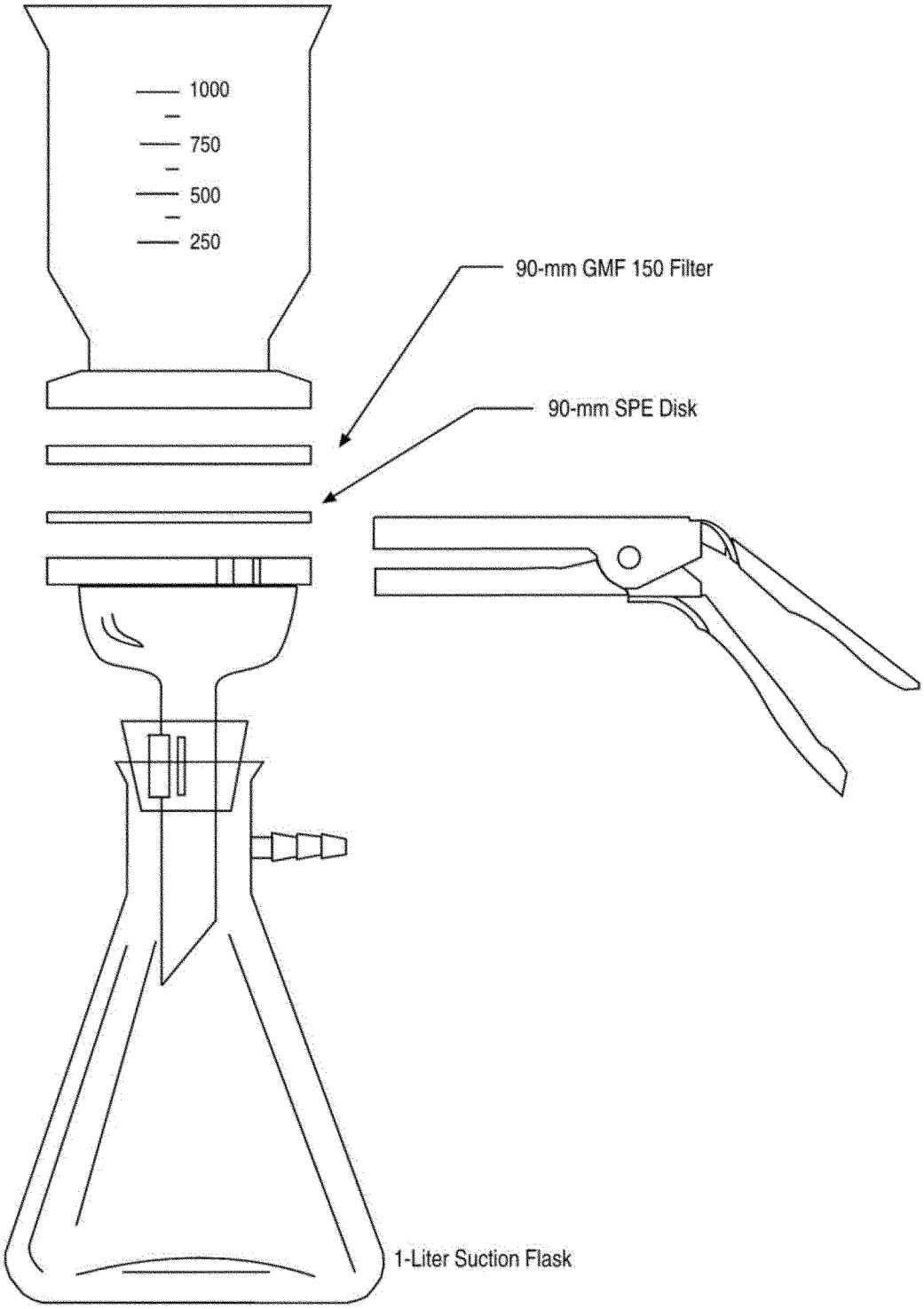


Figure 2 Disk-based solid-phase extraction apparatus

23. Glossary

These definitions and purposes are specific to this method but have been conformed to common usage to the extent possible.

23.1 Units of weight and measure and their abbreviations.

23.1.1 Symbols

°C degrees Celsius
µg microgram
µL microliter
< less than
≤ less than or equal to
> greater than
% percent

23.1.2 Abbreviations (in alphabetical order)

cm centimeter
g gram

hr hour
ID inside diameter
in. inch
L liter
M molar solution—one mole or gram molecular weight of solute in one liter of solution
mg milligram
min minute
mL milliliter
mm millimeter
N Normality—one equivalent of solute in one liter of solution
ng nanogram
psia pounds-per-square inch absolute
psig pounds-per-square inch gauge
v/v volume per unit volume
w/v weight per unit volume

23.2 Definitions and acronyms (in alphabetical order)

Analyte—A compound or mixture of compounds (*e.g.,* PCBs) tested for by this method. The analytes are listed in Tables 1 and 2.

Analytical batch—The set of samples analyzed on a given instrument during a 24-hour period that begins and ends with calibration verification (Sections 7.8 and 13). See also ''Extraction batch.''

Blank (method blank; laboratory blank)—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

Calibration factor (CF)—See Section 7.5.1.

Calibration standard—A solution prepared from stock solutions and/or a secondary standards and containing the analytes of interest, surrogates, and internal standards. This standard is used to model the response of the GC instrument against analyte concentration.

Calibration verification—The process of confirming that the response of the analytical system remains within specified limits of the calibration.

Calibration verification standard—The combined QC standard (Section 7.7) used to verify calibration (Section 13.5) and for LCS tests (Section 8.4).

Extraction Batch—A set of up to 20 field samples (not including QC samples) started through the extraction process in a given 24-hour shift. Each extraction batch of 20 or fewer samples must be accompanied by a blank (Section 8.5), a laboratory control sample (LCS, Section 8.4), a matrix spike and duplicate (MS/MSD; Section 8.3), resulting in a minimum of five samples (1 field sample, 1 blank, 1 LCS, 1 MS, and 1 MSD) and a maximum of 24 samples (20 field samples, 1 blank, 1 LCS, 1 MS, and 1 MSD) for the batch. If greater than 20 samples are to be extracted in a 24-hour shift, the samples must be separated into extraction batches of 20 or fewer samples.

Field Duplicates—Two samples collected at the same time and place under identical conditions, and treated identically throughout field and laboratory procedures. Results of analyses the field duplicates provide an estimate of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

Field blank—An aliquot of reagent water or other reference matrix that is placed in a sample container in the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample. See also ''Blank.''

GC—Gas chromatograph or gas chromatography

Gel-permeation chromatography (GPC)—A form of liquid chromatography in which the analytes are separated based on exclusion from the solid phase by size.

Internal standard—A compound added to an extract or standard solution in a known amount and used as a reference for quantitation of the analytes of interest and surrogates. Also see Internal standard quantitation.

Internal standard quantitation—A means of determining the concentration of an analyte of interest (Tables 1 and 2) by reference to a compound not expected to be found in a sample.

IDC—Initial Demonstration of Capability (Section 8.2); four aliquots of a reference matrix spiked with the analytes of interest and analyzed to establish the ability of the laboratory to generate acceptable precision and recovery. An IDC is performed prior to the first time this method is used and any time the method or instrumentation is modified.

Laboratory Control Sample (LCS; laboratory fortified blank; Section 8.4)—An aliquot of reagent water spiked with known quantities of the analytes of interest and surrogates. The LCS is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

Laboratory Fortified Sample Matrix—See Matrix spike.

Laboratory reagent blank—See blank.

Matrix spike (MS) and matrix spike duplicate (MSD) (laboratory fortified sample matrix and duplicate)—Two aliquots of an environmental sample to which known quantities of the analytes of interest and surrogates are added in the laboratory. The MS/MSD are prepared and analyzed exactly like a field sample. Their purpose is to quantify any additional bias and imprecision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations.

May—This action, activity, or procedural step is neither required nor prohibited.

May not—This action, activity, or procedural step is prohibited.

Method detection limit (MDL)—A detection limit determined by the procedure at 40 CFR part 136, appendix B. The MDLs determined by EPA are listed in Tables 1 and 2. As noted in Sec. 1.6, use the MDLs in Tables 1 and 2 in conjunction with current MDL data from the laboratory actually analyzing samples to assess the sensitivity of this procedure relative to project objectives and regulatory requirements (where applicable).

Minimum level (ML)—The term ''minimum level'' refers to either the sample concentration equivalent to the lowest calibration point in a method or a multiple of the method detection limit (MDL), whichever is higher. Minimum levels may be obtained in several ways: They may be published in a method; they may be based on the lowest acceptable calibration point used by a laboratory; or they may be calculated by multiplying the MDL in a method, or the MDL determined by a laboratory, by a factor of 3. For the purposes of NPDES compliance monitoring, EPA considers the following terms to be synonymous: ''quantitation limit,'' ''reporting limit,'' and ''minimum level.''

MS—Mass spectrometer or mass spectrometry.

Must—This action, activity, or procedural step is required.

Preparation blank—See blank.

Quality control sample (QCS)—A sample containing analytes of interest at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independent of the normal preparation process.

Reagent water—Water demonstrated to be free from the analytes of interest and potentially interfering substances at the MDLs for the analytes in this method.

Regulatory compliance limit—A limit on the concentration or amount of a pollutant or contaminant specified in a nationwide standard, in a permit, or otherwise established by a regulatory/control authority.

Relative standard deviation (RSD)—The standard deviation times 100 divided by the mean. Also termed ''coefficient of variation.''

RF—Response factor. See Section 7.6.2.

RPD—Relative percent difference.

RSD—See relative standard deviation.

Safety Data Sheet (SDS)—Written information on a chemical's toxicity, health hazards, physical properties, fire, and reactivity, including storage, spill, and handling precautions that meet the requirements of OSHA, 29 CFR 1910.1200(g) and appendix D to § 1910.1200. United Nations Globally Harmonized System of Classification and Labelling of Chemicals (GHS), third revised edition, United Nations, 2009.

Should—This action, activity, or procedural step is suggested but not required.

SPE—Solid-phase extraction; a sample extraction or extract cleanup technique in which an analyte is selectively removed from a sample or extract by passage over or through a material capable of reversibly adsorbing the analyte.

Stock solution—A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

Surrogate—A compound unlikely to be found in a sample, which is spiked into the sample in a known amount before extraction, and which is quantified with the same procedures used to quantify other sample components. The purpose of the surrogate is to monitor method performance with each sample.

* * * * *

Method 611—Haloethers

1. Scope and Application

1.1 This method covers the determination of certain haloethers. The following parameters can be determined by this method:

Parameter	STORET No.	CAS No.
Bis(2-chloroethyl) ether	34273	111–44–4
Bis(2-chloroethoxy) methane	34278	111–91–1
2, 2′-oxybis (1-chloropropane)	34283	108–60–1
4-Bromophenyl phenyl ether	34636	101–55–3
4-Chlorophenyl phenyl either	34641	7005–72–3

* * * * *

Method 624.1—Purgeables by GC/MS

1. Scope and Application

1.1 This method is for determination of purgeable organic pollutants in industrial discharges and other environmental samples by gas chromatography combined with mass spectrometry (GC/MS), as provided under 40 CFR 136.1. This revision is based on previous protocols (References 1–3), on the revision promulgated October 26, 1984 (49 FR 43234), and on an interlaboratory method validation study (Reference 4). Although this method was validated through an interlaboratory study conducted more than 29 years ago, the fundamental chemistry principles used in this method remain sound and continue to apply.

1.2 The analytes that may be qualitatively and quantitatively determined using this method and their CAS Registry numbers are listed in Table 1. The method may be extended to determine the analytes listed in Table 2; however, poor purging efficiency or gas chromatography of some of these analytes may make quantitative determination difficult. For example, an elevated temperature may be required to purge some analytes from water. If an elevated temperature is used, calibration and all quality control (QC) tests must be performed at the elevated temperature. EPA encourages the use of this method to determine additional compounds amenable to purge-and-trap GC/MS.

1.3 The large number of analytes in Tables 1 and 2 of this method makes testing difficult if all analytes are determined simultaneously. Therefore, it is necessary to determine and perform QC tests for ''analytes of interest'' only. Analytes of interest are those required to be determined by a regulatory/control authority or in a permit, or by a client. If a list of analytes is not specified, the analytes in Table 1 must be determined, at a minimum, and QC testing must be performed for these analytes. The analytes in Table 1 and some of the analytes in Table 2 have been identified as Toxic Pollutants (40 CFR 401.15), expanded to a list of Priority Pollutants (40 CFR part 423, appendix A).

1.4 Method detection limits (MDLs; Reference 5) for the analytes in Table 1 are listed in that table. These MDLs were determined in reagent water (Reference 6). Advances in analytical technology, particularly the use of capillary (open-tubular) columns, allowed laboratories to routinely achieve MDLs for the analytes in this method that are 2–10 times lower than those in the version promulgated in 1984 (40 FR 43234). The MDL for a specific wastewater may differ from those listed, depending on the nature of interferences in the sample matrix.

1.4.1 EPA has promulgated this method at 40 CFR part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described in Section 13.2 are focused on such monitoring needs and may not be relevant to other uses of the method.

1.4.2 This method includes ''reporting limits'' based on EPA's ''minimum level'' (ML) concept (see the glossary in Section 20). Table 1 contains MDL values and ML values for many of the analytes. The MDL for an analyte in a specific wastewater may differ from that listed in Table 1, depending upon the nature of interferences in the sample matrix.

1.5 This method is performance-based. It may be modified to improve performance (*e.g.,* to overcome interferences or improve the accuracy of results) provided all performance requirements are met.

1.5.1 Examples of allowed method modifications are described at 40 CFR 136.6. Other examples of allowed modifications specific to this method are described in Section 8.1.2.

1.5.2 Any modification beyond those expressly allowed at 40 CFR 136.6 or in Section 8.1.2 of this method shall be considered a major modification that is subject to application and approval of an alternate test procedure under 40 CFR 136.4 and 136.5.

1.5.3 For regulatory compliance, any modification must be demonstrated to produce results equivalent or superior to results produced by this method when applied to relevant wastewaters (Section 8.3).

1.6 This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge-and-trap system and a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure in Section 8.2.

1.7 Terms and units of measure used in this method are given in the glossary at the end of the method.

2. Summary of Method

2.1 A gas is bubbled through a measured volume of water in a specially-designed purging chamber (Figure 1). The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the purgeables are trapped (Figure 2). After purging is completed, the trap is heated and backflushed with the gas to desorb the purgeables onto a gas chromatographic column (Figures 3 and 4). The column is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

2.2 Different sample sizes in the range of 5–25 mL are allowed in order to meet differing sensitivity requirements. Calibration and QC samples must have the same volume as field samples.

3. Interferences

3.1 Impurities in the purge gas, organic compounds outgassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by analyzing blanks as described in Section 8.5. Fluoropolymer tubing, fittings, and thread sealant should be used to avoid contamination.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. Protect samples from sources of volatiles during collection, shipment, and storage. A reagent water field blank carried through sampling and analysis can serve as a check on such contamination.

3.3 Contamination by carry-over can occur whenever high level and low level samples are analyzed sequentially. To reduce the potential for carry-over, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a blank to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high purgeable levels, it may be necessary to wash the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105 °C oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required. Screening samples at high dilution may prevent introduction of contaminants into the system.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of safety data sheets (SDSs, OSHA, 29 CFR 1910.1200(g)) should also be made available to all personnel involved in sample handling and chemical analysis. Additional references to laboratory safety are available and have been identified (References 7–9) for the information of the analyst.

4.2. The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: Benzene; carbon tetrachloride; chloroform; 1,4-dichlorobenzene; 1,2-dichloroethane; 1,2-dichloropropane; methylene chloride; tetrachloroethylene; trichloroethylene; and vinyl chloride. Primary standards of these toxic compounds should be prepared in a chemical fume hood, and a NIOSH/MESA approved toxic gas respirator should be worn when handling high concentrations of these compounds.

4.3 This method allows the use of hydrogen as a carrier gas in place of helium (Section 5.3.1.2). The laboratory should take the necessary precautions in dealing with hydrogen, and should limit hydrogen flow at the source to prevent buildup of an explosive mixture of hydrogen in air.

5. Apparatus and Materials

Note: Brand names, suppliers, and part numbers are cited for illustration purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here. Demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory. Suppliers for equipment and materials in this method may be found through an on-line search.

5.1 Sampling equipment for discrete sampling.

5.1.1 Vial—25 or 40 mL capacity, or larger, with screw cap with a hole in the center (Pierce #13075 or equivalent). Unless pre-cleaned, detergent wash, rinse with tap and reagent water, and dry at 105 °C before use.

5.1.2 Septum—Fluoropolymer-faced silicone (Pierce #12722 or equivalent). Unless pre-cleaned, detergent wash, rinse with tap and reagent water, and dry at 105 ± 5 °C for one hour before use.

5.2 Purge-and-trap system—The purge-and-trap system consists of three separate pieces of equipment: A purging device, trap, and desorber. Several complete systems are commercially available. Any system that meets the performance requirements in this method may be used.

5.2.1 The purging device should accept 5- to 25-mL samples with a water column at least 3 cm deep. The purge gas must pass though the water column as finely divided bubbles. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging device illustrated in Figure 1 meets these design criteria. Purge devices of a different volume may be used so long as the performance requirements in this method are met.

5.2.2 The trap should be at least 25 cm long and have an inside diameter of at least 0.105 in. The trap should be packed to contain the following minimum lengths of adsorbents: 1.0 cm of methyl silicone coated packing (Section 6.3.2), 15 cm of 2,6-diphenylene oxide polymer (Section 6.3.1), and 8 cm of silica gel (Section 6.3.3). The minimum specifications for the trap are illustrated in Figure 2. A trap with different dimensions and packing materials is acceptable so long as the performance requirements in this method are met.

5.2.3 The desorber should be capable of rapidly heating the trap to the temperature necessary to desorb the analytes of interest, and of maintaining

this temperature during desorption. The trap should not be heated higher than the maximum temperature recommended by the manufacturer. The desorber illustrated in Figure 2 meets these design criteria.

5.2.4 The purge-and-trap system may be assembled as a separate unit or coupled to a gas chromatograph as illustrated in Figures 3 and 4.

5.3 GC/MS system.

5.3.1 Gas chromatograph (GC)—An analytical system complete with a temperature programmable gas chromatograph and all required accessories, including syringes and analytical columns. Autosamplers designed for purge-and-trap analysis of volatiles also may be used.

5.3.1.1 Injection port—Volatiles interface, split, splitless, temperature programmable split/splitless (PTV), large volume, on-column, backflushed, or other.

5.3.1.2 Carrier gas—Data in the tables in this method were obtained using helium carrier gas. If another carrier gas is used, analytical conditions may need to be adjusted for optimum performance, and calibration and all QC tests must be performed with the alternate carrier gas. See Section 4.3 for precautions regarding the use of hydrogen as a carrier gas.

5.3.2 GC column—See the footnote to Table 3. Other columns or column systems may be used provided all requirements in this method are met.

5.3.3 Mass spectrometer—Capable of repetitively scanning from 35–260 Daltons (amu) every 2 seconds or less, utilizing a 70 eV (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all criteria in Table 4 when 50 ng or less of 4-bromofluorobenzene (BFB) is injected through the GC inlet. If acrolein, acrylonitrile, chloromethane, and vinyl chloride are to be determined, it may be necessary to scan from below 25 Daltons to measure the peaks in the 26—35 Dalton range for reliable identification.

5.3.4 GC/MS interface—Any GC to MS interface that meets all performance requirements in this method may be used.

5.3.5 Data system—A computer system must be interfaced to the mass spectrometer that allows continuous acquisition and storage of mass spectra throughout the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific m/z's (masses) and plotting m/z abundances versus time or scan number. This type of plot is defined as an extracted ion current profile (EICP). Software must also be available that allows integrating the abundance at any EICP between specified time or scan number limits.

5.4 Syringes—Graduated, 5–25 mL, glass hypodermic with Luerlok tip, compatible with the purging device.

5.5 Micro syringes—Graduated, 25–1000 µL, with 0.006 in. ID needle.

5.6 Syringe valve—Two-way, with Luer ends.

5.7 Syringe—5 mL, gas-tight with shut-off valve.

5.8 Bottle—15 mL, screw-cap, with Teflon cap liner.

5.9 Balance—Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water—Reagent water is defined as water in which the analytes of interest and interfering compounds are not detected at the MDLs of the analytes of interest. It may be generated by passing deionized water, distilled water, or tap water through a carbon bed, passing the water through a water purifier, or heating the water to between 90 and 100 °C while bubbling contaminant free gas through it for approximately 1 hour. While still hot, transfer the water to screw-cap bottles and seal with a fluoropolymer-lined cap.

6.2 Sodium thiosulfate—(ACS) Granular.

6.3 Trap materials.

6.3.1 2,6-Diphenylene oxide polymer—Tenax, 60/80 mesh, chromatographic grade, or equivalent.

6.3.2 Methyl silicone packing—3% OV–1 on Chromosorb-W, 60/80 mesh, or equivalent.

6.3.3 Silica gel—35/60 mesh, Davison, Grade-15 or equivalent.

Other trap materials are acceptable if performance requirements in this method are met.

6.4 Methanol—Demonstrated to be free from the target analytes and potentially interfering compounds.

6.5 Stock standard solutions—Stock standard solutions may be prepared from pure materials, or purchased as certified solutions. Traceability must be to the National Institute of Standards and Technology (NIST) or other national standard. Stock solution concentrations alternate to those below may be used. Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate. Because some of the compounds in this method are known to be toxic, primary dilutions should be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations of neat materials are handled. The following procedure may be used to prepare standards from neat materials:

6.5.1 Place about 9.8 mL of methanol in a 10-mL ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

6.5.2 Add the assayed reference material.

6.5.2.1 Liquids—Using a 100 µL syringe, immediately add two or more drops of assayed reference material to the flask. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask. Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in µg/µL from the net gain in weight.

6.5.2.2 Gases—To prepare standards for any of compounds that boil below 30 °C, fill a 5-mL valved gas-tight syringe with reference standard vapor to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the vapor above the surface of the liquid (the vapor will rapidly dissolve in the methanol). Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in µg/µL from the net gain in weight.

6.5.3 When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.5.4 Prepare fresh standards weekly for the gases and 2-chloroethylvinyl ether. All standards should be replaced after one month, or sooner if the concentration of an analyte changes by more than 10 percent.

Note: 2-Chloroethylvinyl ether has been shown to be stable for as long as one month if prepared as a separate standard, and the other analytes have been shown to be stable for as long as 2 months if stored at less than −10 °C with minimal headspace in sealed, miniature inert-valved vials.

6.6 Secondary dilution standards—Using stock solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed. Secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 7.3.2 will bracket the working range of the analytical system.

6.7 Surrogate standard spiking solution—Select a minimum of three surrogate compounds from Table 5. The surrogates selected should match the purging characteristics of the analytes of interest as closely as possible. Prepare a stock standard solution for each

surrogate in methanol as described in Section 6.5, and prepare a solution for spiking the surrogates into all blanks, LCSs, and MS/MSDs. The spiking solution should be prepared such that spiking a small volume will result in surrogate concentrations near the mid-point of the calibration range. For example, adding 10 µL of a spiking solution containing the surrogates at a concentration of 15 µg/mL in methanol to a 5-mL aliquot of water would result in a concentration of 30 µg/L for each surrogate. Other surrogate concentrations may be used.

6.8 BFB standard—Prepare a solution of BFB in methanol as described in Sections 6.5 and 6.6. The solution should be prepared such that an injection or purging from water will result in introduction of ≤50 ng into the GC. BFB may be included in a mixture with the internal standards and/or surrogates.

6.9 Quality control check sample concentrate—See Section 8.2.1.

6.10 Storage—When not being used, store standard solutions (Sections 6.5–6.9) at −10 to −20 °C, protected from light, in fluoropolymer-sealed glass containers with minimal headspace.

7. Calibration

7.1 Assemble a purge-and-trap system that meets the specifications in Section 5.2. Prior to first use, condition the trap overnight at 180 °C by backflushing with gas at a flow rate of at least 20 mL/min. Condition the trap daily prior to use.

7.2 Connect the purge-and-trap system to the gas chromatograph. The gas chromatograph should be operated using temperature and flow rate conditions equivalent to those given in the footnotes to Table 3. Alternative temperature and flow rate conditions may be used provided that performance requirements in this method are met.

7.3 Internal standard calibration.

7.3.1 Internal standards.

7.3.1.1 Select three or more internal standards similar in chromatographic behavior to the compounds of interest. Suggested internal standards are listed in Table 5. Use the base peak m/z as the primary m/z for quantification of the standards. If interferences are found at the base peak, use one of the next two most intense m/z's for quantitation. Demonstrate that measurement of the internal standards are not affected by method or matrix interferences.

7.3.1.2 To assure accurate analyte identification, particularly when selected ion monitoring (SIM) is used, it may be advantageous to include more internal standards than those suggested in Section 7.3.1.1. An analyte will be located most accurately if its retention time relative to an internal standard is in the range of 0.8 to 1.2.

7.3.1.3 Prepare a stock standard solution for each internal standard surrogate in methanol as described in Section 6.5, and prepare a solution for spiking the internal standards into all blanks, LCSs, and MS/MSDs. The spiking solution should be prepared such that spiking a small volume will result in internal standard concentrations near the mid-point of the calibration range. For example, adding 10 µL of a spiking solution containing the internal standards at a concentration of 15 µg/mL in methanol to a 5-mL aliquot of water would result in a concentration of 30 µg/L for each internal standard. Other concentrations may be used. The internal standard solution and the surrogate standard spiking solution (Section 6.7) may be combined, if desired. Store the solution at <6 °C in fluoropolymer-sealed glass containers with a minimum of headspace. Replace the solution after 1 month, or more frequently if comparison with QC standards indicates a problem.

7.3.2 Calibration.

7.3.2.1 Calibration standards.

7.3.2.1.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest by adding appropriate volumes of one or more stock standards to a fixed volume (*e.g.,* 40 mL) of reagent water in volumetric glassware. Fewer levels may be necessary for some analytes based on the sensitivity of the MS. The concentration of the lowest calibration standard for an analyte should be at or near the ML value in Table 1 for an analyte listed in that table. The ML value may be rounded to a whole number that is more convenient for preparing the standard, but must not exceed the ML values listed in Table 1 for those analytes which list ML values. Alternatively, the laboratory may establish the ML for each analyte based on the concentration of the lowest calibration standard in a series of standards obtained from a commercial vendor, again, provided that the ML values does not exceed the MLs in Table 1, and provided that the resulting calibration meets the acceptance criteria in Section 7.3.4, based on the RSD, RSE, or R^2.

The concentrations of the higher standards should correspond to the expected range of concentrations found in real samples, or should define the working range of the GC/MS system for full-scan and/or SIM operation, as appropriate. A minimum of six concentration levels is required for a second order, non-linear (*e.g.,* quadratic; $ax^2 + bx + c$) calibration. Calibrations higher than second order are not allowed.

7.3.2.1.2 To each calibration standard or standard mixture, add a known constant volume of the internal standard spiking solution (Section 7.3.1.3) and surrogate standard spiking solution (Section 6.7) or the combined internal standard solution and surrogate spiking solution (Section 7.3.1.3). Aqueous standards may be stored up to 24 hours, if held in sealed vials with zero headspace as described in Section 9.1. If not so stored, they must be discarded after one hour.

7.3.2.2 Prior to analysis of the calibration standards, analyze the BFB standard (Section 6.8) and adjust the scan rate of the MS to produce a minimum of 5 mass spectra across the BFB GC peak, but do not exceed 2 seconds per scan. Adjust instrument conditions until the BFB criteria in Table 4 are met.

Note: The BFB spectrum may be evaluated by summing the intensities of the m/z's across the GC peak, subtracting the background at each m/z in a region of the chromatogram within 20 scans of but not including any part of the BFB peak. The BFB spectrum may also be evaluated by fitting a Gaussian to each m/z and using the intensity at the maximum for each Gaussian, or by integrating the area at each m/z and using the integrated areas. Other means may be used for evaluation of the BFB spectrum so long as the spectrum is not distorted to meet the criteria in Table 4.

7.3.2.3 Analyze the mid-point standard and enter or review the retention time, relative retention time, mass spectrum, and quantitation m/z in the data system for each analyte of interest, surrogate, and internal standard. If additional analytes (Table 2) are to be quantified, include these analytes in the standard. The mass spectrum for each analyte must be comprised of a minimum of 2 m/z's; 3 to 5 m/z's assure more reliable analyte identification. Suggested quantitation m/z's are shown in Table 6 as the primary m/z. For analytes in Table 6 that do not have a secondary m/z, acquire a mass spectrum and enter one or more secondary m/z's for more reliable identification. If an interference occurs at the primary m/z, use one of the secondary m/z's or an alternate m/z. A single m/z only is required for quantitation.

7.3.2.4 For SIM operation, determine the analytes in each descriptor, the quantitation m/z for each analyte (the quantitation m/z can be the same as for full-scan operation; Section 7.3.2.3), the dwell time on each m/z for each analyte,

and the beginning and ending retention time for each descriptor. Analyze the verification standard in scan mode to verify m/z's and establish retention times for the analytes. There must be a minimum of two m/z's for each analyte to assure analyte identification. To maintain sensitivity, the number of m/z's in a descriptor should be limited. For example, for a descriptor with 10 m/z's and a chromatographic peak width of 5 sec, a dwell time of 100 ms at each m/z would result in a scan time of 1 second and provide 5 scans across the GC peak. The quantitation m/z will usually be the most intense peak in the mass spectrum. The quantitation m/z and dwell time may be optimized for each analyte. However, if a GC peak spans two (or more) descriptors, the dwell time and cycle time (scans/sec) should be set to the same value in both segments in order to maintain equivalent response. The acquisition table used for SIM must take into account the mass defect (usually less than 0.2 Dalton) that can occur at each m/z monitored.

7.3.2.5 For combined scan and SIM operation, set up the scan segments and descriptors to meet requirements in Sections 7.3.2.2–7.3.2.4.

7.3.3 Analyze each calibration standard according to Section 10 and tabulate the area at the quantitation m/z against concentration for each analyte of interest, surrogate, and internal standard. Calculate the response factor (RF) for each compound at each concentration using Equation 1.

$$RF = \frac{(A_s x C_{is})}{(A_{is} x C_s)} \qquad \text{Equation 1}$$

Where:

A_s = Area of the characteristic m/z for the analyte to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard (µg/L).

C_s = Concentration of the analyte to be measured (µg/L).

7.3.4 Calculate the mean (average) and relative standard deviation (RSD) of the response factors. If the RSD is less than 35%, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to fit a linear or quadratic regression of response ratios, A_s/A_{is}, vs. concentration ratios Cs/Cis. If used, the regression must be weighted inversely proportional to concentration (1/C). The coefficient of determination (R^2) of the weighted regression must be greater than 0.920 (this value roughly corresponds to the RSD limit of 35%). Alternatively, the relative standard error (Reference 10) may be used as an acceptance criterion. As with the RSD, the RSE must be less than 35%. If an RSE less than 35% cannot be achieved for a quadratic regression, system performance is unacceptable, and the system must be adjusted and re-calibrated.

Note: Using capillary columns and current instrumentation, it is quite likely that a laboratory can calibrate the target analytes in this method and achieve a linearity metric (either RSD or RSE) well below 35%. Therefore, laboratories are permitted to use more stringent acceptance criteria for calibration than described here, for example, to harmonize their application of this method with those from other sources.

7.4 Calibration verification—Because the analytical system is calibrated by purge of the analytes from water, calibration verification is performed using the laboratory control sample (LCS). See Section 8.4 for requirements for calibration verification using the LCS, and the Glossary for further definition.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and ongoing analysis of spiked samples and blanks to evaluate and document data quality (40 CFR 136.7). The laboratory must maintain records to document the quality of data generated. Results of ongoing performance tests are compared with established QC acceptance criteria to determine if the results of analyses meet performance requirements of this method. When results of spiked samples do not meet the QC acceptance criteria in this method, a quality control check sample (laboratory control sample; LCS) must be analyzed to confirm that the measurements were performed in an in-control mode of operation. A laboratory may develop its own performance criteria (as QC acceptance criteria), provided such criteria are as or more restrictive than the criteria in this method.

8.1.1 The laboratory must make an initial demonstration of capability (DOC) to generate acceptable precision and recovery with this method. This demonstration is detailed in Section 8.2.

8.1.2 In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory is permitted certain options (Section 1.5 and 40 CFR 136.6(b)) to improve separations or lower the costs of measurements. These options may include an alternate purge-and-trap device, and changes in both column and type of mass spectrometer (see 40 CFR 136.6(b)(4)(xvi)). Alternate determinative techniques, such as substitution of spectroscopic or immunoassay techniques, and changes that degrade method performance, are not allowed. If an analytical technique other than GC/MS is used, that technique must have a specificity equal to or greater than the specificity of GC/MS for the analytes of interest. The laboratory is also encouraged to participate in inter-comparison and performance evaluation studies (see Section 8.9).

8.1.2.1 Each time a modification is made to this method, the laboratory is required to repeat the procedure in Section 8.2. If the detection limit of the method will be affected by the change, the laboratory must demonstrate that the MDLs (40 CFR part 136, appendix B) are lower than one-third the regulatory compliance limit, or at least as low as the MDLs listed in this method, whichever are greater. If calibration will be affected by the change, the instrument must be recalibrated per Section 7. Once the modification is demonstrated to produce results equivalent or superior to results produced by this method, that modification may be used routinely thereafter, so long as the other requirements in this method are met (*e.g.,* matrix spike/matrix spike duplicate recovery and relative percent difference).

8.1.2.1.1 If a modification is to be applied to a specific discharge, the laboratory must prepare and analyze matrix spike/matrix spike duplicate (MS/MSD) samples (Section 8.3) and LCS samples (Section 8.4). The laboratory must include internal standards and surrogates (Section 8.7) in each of the samples. The MS/MSD and LCS samples must be fortified with the analytes of interest (Section 1.3.). If the modification is for nationwide use, MS/

MSD samples must be prepared from a minimum of nine different discharges (See Section 8.1.2.1.2), and all QC acceptance criteria in this method must be met. This evaluation only needs to be performed once, other than for the routine QC required by this method (for example it could be performed by the vendor of the alternate materials) but any laboratory using that specific material must have the results of the study available. This includes a full data package with the raw data that will allow an independent reviewer to verify each determination and calculation performed by the laboratory (see Section 8.1.2.2.5, items a–l).

8.1.2.1.2 Sample matrices on which MS/MSD tests must be performed for nationwide use of an allowed modification:

(a) Effluent from a POTW

(b) ASTM D5905 Standard Specification for Substitute Wastewater

(c) Sewage sludge, if sewage sludge will be in the permit

(d) ASTM D1141 Standard Specification for Substitute Ocean Water, if ocean water will be in the permit

(e) Untreated and treated wastewaters up to a total of nine matrix types (see *http:water.epa.gov/scitech/wastetech/guide/industry.cfm*) for a list of industrial categories with existing effluent guidelines).

At least one of the above wastewater matrix types must have at least one of the following characteristics:

(i) Total suspended solids greater than 40 mg/L

(ii) Total dissolved solids greater than 100 mg/L

(iii) Oil and grease greater than 20 mg/L

(iv) NaCl greater than 120 mg/L

(v) CaCO3 greater than 140 mg/L

The interim acceptance criteria for MS, MSD recoveries that do not have recovery limits specified in Table 7, and recoveries for surrogates that do not have recovery limits specified in Table 7, must be no wider than 60–140%, and the relative percent difference (RPD) of the concentrations in the MS and MSD that do not have RPD limits specified in Table 7 must be less than 30%. Alternatively, the laboratory may use the laboratory's in-house limits if they are tighter.

(f) A proficiency testing (PT) sample from a recognized provider, in addition to tests of the nine matrices (Section 8.1.2.1.1).

8.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

8.1.2.2.1 The names, titles, street addresses, telephone numbers, and email addresses of the analyst(s) that performed the analyses and modification, and of the quality control officer that witnessed and will verify the analyses and modifications.

8.1.2.2.2 A list of analytes, by name and CAS Registry Number.

8.1.2.2.3 A narrative stating reason(s) for the modifications.

8.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

(a) Calibration (Section 7).

(b) Calibration verification/LCS (Section 8.4).

(c) Initial demonstration of capability (Section 8.2).

(d) Analysis of blanks (Section 8.5).

(e) Matrix spike/matrix spike duplicate analysis (Section 8.3).

(f) Laboratory control sample analysis (Section 8.4).

8.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

(a) Sample numbers and other identifiers.

(b) Analysis dates and times.

(c) Analysis sequence/run chronology.

(d) Sample volume (Section 10).

(e) Sample dilution (Section 13.2).

(f) Instrument and operating conditions.

(g) Column (dimensions, material, etc).

(h) Operating conditions (temperature program, flow rate, etc).

(i) Detector (type, operating conditions, etc).

(j) Chromatograms, mass spectra, and other recordings of raw data.

(k) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.

(l) A written Standard Operating Procedure (SOP).

8.1.2.2.6 The individual laboratory wishing to use a given modification must perform the start-up tests in Section 8.1.2 (*e.g.,* DOC, MDL), with the modification as an integral part of this method prior to applying the modification to specific discharges. Results of the DOC must meet the QC acceptance criteria in Table 7 for the analytes of interest (Section 1.3), and the MDLs must be equal to or lower than the MDLs in Table3 for the analytes of interest

8.1.3 Before analyzing samples, the laboratory must analyze a blank to demonstrate that interferences from the analytical system, labware, and reagents are under control. Each time a batch of samples is analyzed or reagents are changed, a blank must be analyzed as a safeguard against laboratory contamination. Requirements for the blank are given in Section 8.5.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of one sample, in duplicate, with the batch of samples run during a given 12-hour shift (see the note at Section 8.4). The laboratory must also spike and analyze, in duplicate, a minimum of 5% of all samples from a given site or discharge to monitor and evaluate method and laboratory performance on the sample matrix. The batch and site/discharge samples may be the same. The procedure for spiking and analysis is given in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through analysis of a quality control check sample (laboratory control sample, LCS; on-going precision and recovery sample, OPR) that the measurement system is in control. This procedure is given in Section 8.4.

8.1.6 The laboratory should maintain performance records to document the quality of data that is generated. This procedure is given in Section 8.8.

8.1.7 The large number of analytes tested in performance tests in this method present a substantial probability that one or more will fail acceptance criteria when many analytes are tested simultaneously, and a re-test is allowed if this situation should occur. If, however, continued re-testing results in further repeated failures, the laboratory should document the failures (*e.g.,* as qualifiers on results) and either avoid reporting results for analytes that failed or report the problem and failures with the data. Failure to report does not relieve a discharger or permittee of reporting timely results. Results for regulatory compliance must be accompanied by QC results that meet all acceptance criteria.

8.2 Initial demonstration of capability (DOC)—To establish the ability to generate acceptable recovery and precision, the laboratory must perform the DOC in Sections 8.2.1 through 8.2.6 for the analytes of interest. The laboratory must also establish MDLs for the analytes of interest using the MDL procedure at 40 CFR part 136, appendix B. The laboratory's MDLs must be equal to or lower than those listed in Table 1 for those analytes which list MDL values, or lower than one-third the regulatory compliance limit, whichever is greater. For MDLs not listed in Table 1, the laboratory must determine the MDLs using the MDL procedure at 40 CFR part 136, appendix B under the same conditions

used to determine the MDLs for the analytes listed in Table 1. All procedures used in the analysis must be included in the DOC.

8.2.1 For the DOC, a QC check sample concentrate containing each analyte of interest (Section 1.3) is prepared in methanol. The QC check sample concentrate must be prepared independently from those used for calibration, but may be from the same source as the second-source standard used for calibration verification/LCS (Sections 7.4 and 8.4). The concentrate should produce concentrations of the analytes of interest in water at the mid-point of the calibration range, and may be at the same concentration as the LCS (Section 8.4).

Note: QC check sample concentrates are no longer available from EPA.

8.2.2 Using a pipet or micro-syringe, prepare four LCSs by adding an appropriate volume of the concentrate to each of four aliquots of reagent water. The volume of reagent water must be the same as the volume that will be used for the sample, blank (Section 8.5), and MS/MSD (Section 8.3). A volume of 5 mL and a concentration of 20 µg/L were used to develop the QC acceptance criteria in Table 7. An alternative volume and sample concentration may be used, provided that all QC tests are performed and all QC acceptance criteria in this method are met. Also add an aliquot of the surrogate spiking solution (Section 6.7) and internal standard spiking solution (Section 7.3.1.3) to the reagent-water aliquots.

8.2.3 Analyze the four LCSs according to the method beginning in Section 10.

8.2.4 Calculate the average percent recovery ($\bar{x}$) and the standard deviation of the percent recovery (s) for each analyte using the four results.

8.2.5 For each analyte, compare s and $\bar{x}$ with the corresponding acceptance criteria for precision and recovery in Table 7. For analytes in Tables 1 and 2 not listed in Table 7, DOC QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 11 and 12). If s and $\bar{x}$ for all analytes of interest meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If any individual s exceeds the precision limit or any individual $\bar{x}$ falls outside the range for recovery, system performance is unacceptable for that analyte.

Note: The large number of analytes in Tables 1 and 2 present a substantial probability that one or more will fail at least one of the acceptance criteria when many or all analytes are determined simultaneously. Therefore, the analyst is permitted to conduct a ''re-test'' as described in Sec. 8.2.6.

8.2.6 When one or more of the analytes tested fail at least one of the acceptance criteria, repeat the test for only the analytes that failed. If results for these analytes pass, system performance is acceptable and analysis of samples and blanks may proceed. If one or more of the analytes again fail, system performance is unacceptable for the analytes that failed the acceptance criteria. Correct the problem and repeat the test (Section 8.2). See Section 8.1.7 for disposition of repeated failures.

Note: To maintain the validity of the test and re-test, system maintenance and/or adjustment is not permitted between this pair of tests.

8.3 Matrix spike and matrix spike duplicate (MS/MSD)—The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored in duplicate to assess accuracy (recovery and precision). The data user should identify the sample and the analytes of interest (Section 1.3) to be spiked. If direction cannot be obtained, the laboratory must spike at least one sample per batch of samples analyzed on a given 12-hour shift with the analytes in Table 1. Spiked sample results should be reported only to the data user whose sample was spiked, or as requested or required by a regulatory/control authority, or in a permit.

8.3.1 If, as in compliance monitoring, the concentration of a specific analyte will be checked against a regulatory concentration limit, the concentration of the spike should be at that limit; otherwise, the concentration of the spike should be one to five times higher than the background concentration determined in Section 8.3.2, at or near the midpoint of the calibration range, or at the concentration in the LCS (Section 8.4) whichever concentration would be larger.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of the each analyte of interest. If necessary, prepare a new check sample concentrate (Section 8.2.1) appropriate for the background concentration. Spike and analyze two additional sample aliquots, and determine the concentration after spiking (A_1 and A_2) of each analyte. Calculate the percent recoveries (P_1 and P_2) as 100 $(A_1–B)/T$ and 100 $(A_2–B)/T$, where T is the known true value of the spike. Also calculate the relative percent difference (RPD) between the concentrations (A_1 and A_2) as $200|A_1–A_2|/(A_1 + A_2)$. If necessary, adjust the concentrations used to calculate the RPD to account for differences in the volumes of the spiked aliquots.

8.3.3 Compare the percent recoveries (P_1 and P_2) and the RPD for each analyte in the MS/MSD aliquots with the corresponding QC acceptance criteria in Table 7. A laboratory may develop and apply QC acceptance criteria more restrictive than the criteria in Table 6, if desired.

8.3.3.1 If any individual P falls outside the designated range for recovery in either aliquot, or the RPD limit is exceeded, the result for the analyte in the unspiked sample is suspect and may not be reported or used for permitting or regulatory compliance purposes. See Section 8.1.7 for disposition of failures.

8.3.3.2 The acceptance criteria in Table 7 were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the spike to background ratio approaches 5:1 (Reference 13). If spiking is performed at a concentration lower than 20 µg/L, the laboratory must use either the QC acceptance criteria in Table 7, or optional QC acceptance criteria calculated for the specific spike concentration. To use the optional acceptance criteria: (1) Calculate recovery (X′) using the equation in Table 8, substituting the spike concentration (T) for C; (2) Calculate overall precision (S′) using the equation in Table 8, substituting X′ for $\bar{x}$; (3) Calculate the range for recovery at the spike concentration as (100 X′/T) ± 2.44(100 S′/T)% (Reference 4). For analytes of interest in Tables 1 and 2 not listed in Table 7, QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 11 and 12).

8.3.4 After analysis of a minimum of 20 MS/MSD samples for each target analyte and surrogate, the laboratory must calculate and apply in-house QC limits for recovery and RPD of future MS/MSD samples (Section 8.3). The QC limits for recovery are calculated as the mean observed recovery ± 3 standard deviations, and the upper QC limit for RPD is calculated as the mean RPD plus 3 standard deviations of the RPDs. The in-house QC limits must be updated at least every two years and re-established after any major change in the analytical instrumentation or process. At least 80% of the analytes tested in the MS/MSD must have in-house QC acceptance criteria that are tighter than those in

Table 7. If an in-house QC limit for the RPD is greater than the limit in Table 7, then the limit in Table 7 must be used. Similarly, if an in-house lower limit for recovery is below the lower limit in Table 7, then the lower limit in Table 7 must be used, and if an in-house upper limit for recovery is above the upper limit in Table 7, then the upper limit in Table 7 must be used. The laboratory must evaluate surrogate recovery data in each sample against its in-house surrogate recovery limits. The laboratory may use 60–140% as interim acceptance criteria for surrogate recoveries until in-house limits are developed.

8.4 Calibration verification/laboratory control sample (LCS)—The working calibration curve or RF must be verified at the beginning of each 12-hour shift by the measurement of an LCS.

Note: The 12-hour shift begins after analysis of the blank that follows the LCS and ends 12 hours later. The blank is outside of the 12-hour shift. The MS and MSD are treated as samples and are analyzed within the 12-hour shift.

8.4.1 Prepare the LCS by adding QC check sample concentrate (Section 8.2.1) to reagent water. Include all analytes of interest (Section 1.3) in the LCS. The LCS may be the same sample prepared for the DOC (Section 8.2.1). The volume of reagent water must be the same as the volume used for the sample, blank (Section 8.5), and MS/MSD (Section 8.3). Also add an aliquot of the surrogate solution (Section 6.7) and internal standard solution (Section 7.3.1.3). The concentration of the analytes in reagent water should be the same as the concentration in the DOC (Section 8.2.2).

8.4.2 Analyze the LCS prior to analysis of field samples in the batch of samples analyzed during the 12-hour shift (see the Note at Section 8.4). Determine the concentration (A) of each analyte. Calculate the percent recovery (Q) as 100 (A/T) %, where T is the true value of the concentration in the LCS.

8.4.3 Compare the percent recovery (Q) for each analyte with its corresponding QC acceptance criterion in Table 7. For analytes of interest in Tables 1 and 2 not listed in Table 7, use the QC acceptance criteria developed for the MS/MSD (Section 8.3.3.2). If the recoveries for all analytes of interest fall within their respective QC acceptance criteria, analysis of blanks and field samples may proceed. If any individual Q falls outside the range, proceed according to Section 8.4.4.

Note: The large number of analytes in Tables 1–2 present a substantial probability that one or more will fail the acceptance criteria when all analytes are tested simultaneously. Because a re-test is allowed in event of failure (Sections 8.1.7 and 8.4.3), it may be prudent to analyze two LCSs together and evaluate results of the second analysis against the QC acceptance criteria only if an analyte fails the first test.

8.4.4 Repeat the test only for those analytes that failed to meet the acceptance criteria (Q). If these analytes now pass, system performance is acceptable and analysis of blanks and samples may proceed. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, repeat the test using a fresh LCS (Section 8.2.2) or an LCS prepared with a fresh QC check sample concentrate (Section 8.2.1), or perform and document system repair. Subsequent to repair, repeat the calibration verification/LCS test (Section 8.4). If the acceptance criteria for Q cannot be met, re-calibrate the instrument (Section 7). If failure of the LCS indicates a systemic problem with samples analyzed during the 12-hour shift, re-analyze the samples analyzed during that 12-hour shift. See Section 8.1.7 for disposition of repeated failures.

Note: To maintain the validity of the test and re-test, system maintenance and/or adjustment is not permitted between this pair of tests.

8.4.5 After analysis of 20 LCS samples, the laboratory must calculate and apply in-house QC limits for recovery to future LCS samples (Section 8.4). Limits for recovery in the LCS are calculated as the mean recovery ±3 standard deviations. A minimum of 80% of the analytes tested for in the LCS must have QC acceptance criteria tighter than those in Table 7. Many of the analytes and surrogates may not contain recommended acceptance criteria. The laboratory should use 60–140% as interim acceptance criteria for recoveries of spiked analytes and surrogates that do not have recovery limits specified in Table 7, until in-house LCS and surrogate limits are developed. If an in-house lower limit for recovery is lower than the lower limit in Table 7, the lower limit in Table 7 must be used, and if an in-house upper limit for recovery is higher than the upper limit in Table 7, the upper limit in Table 7 must be used.

8.5 Blank—A blank must be analyzed at the beginning of each 12-hour shift to demonstrate freedom from contamination. A blank must also be analyzed after a sample containing a high concentration of an analyte or potentially interfering compound to demonstrate freedom from carry-over.

8.5.1 Spike the internal standards and surrogates into the blank. Analyze the blank immediately after analysis of the LCS (Section 8.4) and prior to analysis of the MS/MSD and samples to demonstrate freedom from contamination.

8.5.2 If any analyte of interest is found in the blank: (1) at a concentration greater than the MDL for the analyte, (2) at a concentration greater than one-third the regulatory compliance limit, or (3) at a concentration greater than one-tenth the concentration in a sample analyzed during the 12-hour shift (Section 8.4), whichever is greater; analysis of samples must be halted and samples affected by the blank must be re-analyzed. Samples must be associated with an uncontaminated blank before they may be reported or used for permitting or regulatory compliance purposes.

8.6 Surrogate recoveries—Spike the surrogates into all samples, blanks, LCSs, and MS/MSDs. Compare surrogate recoveries against the QC acceptance criteria in Table 7. For surrogates in Table 5 without QC acceptance criteria in Table 7, and for other surrogates that may be used by the laboratory, limits must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 11 and 12). If any recovery fails its criteria, attempt to find and correct the cause of the failure. Surrogate recoveries from the blank and LCS may be used as pass/fail criteria by the laboratory or as required by a regulatory authority, or may be used to diagnose problems with the analytical system.

8.7 Internal standard responses.

8.7.1 Calibration verification/LCS—The responses (GC peak heights or areas) of the internal standards in the calibration verification/LCS must be within 50% to 200% (½ to 2x) of their respective responses in the mid-point calibration standard. If they are not, repeat the LCS test using a fresh QC check sample (Section 8.4.1) or perform and document system repair. Subsequent to repair, repeat the calibration verification/LCS test (Section 8.4). If the responses are still not within 50% to 200%, re-calibrate the instrument (Section 7) and repeat the calibration verification/LCS test.

8.7.2 Samples, blanks, and MS/MSDs—The responses (GC peak heights or areas) of the internal standards in each sample, blank, and MS/MSD must be within 50% to 200% (½ to 2x) of its respective response in the most recent LCS. If, as a group, all internal standard are not within this range, perform and document system repair, repeat the calibration verification/LCS test

(Section 8.4), and re-analyze the affected samples. If a single internal standard is not within the 50% to 200% range, use an alternate internal standard for quantitation of the analyte referenced to the affected internal standard.

8.8 As part of the QC program for the laboratory, control charts or statements of accuracy for wastewater samples must be assessed and records maintained periodically (see 40 CFR 136.7(c)(1)(viii)). After analysis of five or more spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{x}$) and the standard deviation of the percent recovery (sp). Express the accuracy assessment as a percent interval from $\bar{x} - 2sp$ to $\bar{x} + 2sp$. For example, if $\bar{x} = 90\%$ and sp = 10%, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each analyte on a regular basis (*e.g.,* after each 5–10 new accuracy measurements).

8.9 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Collect the sample as a grab sample in a glass container having a total volume of at least 25 mL. Fill the sample bottle just to overflowing in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. If needed, collect additional sample(s) for the MS/MSD (Section 8.3).

9.2 Ice or refrigerate samples at <6 °C from the time of collection until analysis, but do not freeze. If residual chlorine is present, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl_2) to the empty sample bottle just prior to shipping to the sampling site. Any method suitable for field use may be employed to test for residual chlorine (Reference 14). Field test kits are also available for this purpose. If sodium thiosulfate interferes in the determination of the analytes, an alternate preservative (*e.g.,* ascorbic acid or sodium sulfite) may be used. If preservative has been added, shake the sample vigorously for one minute. Maintain the hermetic seal on the sample bottle until time of analysis.

9.3 If acrolein is to be determined, analyze the sample within 3 days. To extend the holding time to 14 days, acidify a separate sample to pH 4–5 with HCl using the procedure in Section 9.7.

9.4 Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions (Reference 3). Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. To extend the holding time for aromatic compounds to 14 days, acidify the sample to approximately pH 2 using the procedure in Section 9.7.

9.5 If halocarbons are to be determined, either use the acidified aromatics sample in Section 9.4 or acidify a separate sample to a pH of about 2 using the procedure in Section 9.7. Aqueous samples should not be preserved with acid if the ethers in Table 2, or the alcohols that they would form upon hydrolysis, are of analytes of interest.

9.6 The ethers listed in Table 2 are prone to hydrolysis at pH 2 when a heated purge is used. Aqueous samples should not be acid preserved if these ethers are of interest, or if the alcohols they would form upon hydrolysis are of interest and the ethers are anticipated to present.

9.7 Sample acidification—Collect about 500 mL of sample in a clean container and adjust the pH of the sample to 4–5 for acrolein (Section 9.3), or to about 2 for the aromatic compounds (Section 9.4) by adding 1+1 HCl while swirling or stirring. Check the pH with narrow range pH paper. Fill a sample container as described in Section 9.1. Alternatively, fill a precleaned vial (Section 5.1.1) that contains approximately 0.25 mL of 1+1 HCl with sample as in Section 9.1. If preserved using this alternative procedure, the pH of the sample can be verified to be <2 after some of the sample is removed for analysis. Acidification will destroy 2-chloroethylvinyl ether; therefore, determine 2-chloroethylvinyl ether from the unacidified sample.

9.8 All samples must be analyzed within 14 days of collection (Reference 3), unless specified otherwise in Sections 9.3–9.7.

10. Sample Purging and Gas Chromatography

10.1 The footnote to Table 3 gives the suggested GC column and operating conditions. Included in Table 3 are retention times and MDLs that can be achieved under these conditions. Sections 10.2 through 10.7 suggest procedures that may be used with a manual purge-and-trap system. Autosamplers and other columns or chromatographic conditions may be used if requirements in this method are met.

10.2 Attach the trap inlet to the purging device, and set the purge-and-trap system to purge (Figure 3). Open the syringe valve located on the purging device sample introduction needle.

10.3 Allow the sample to come to ambient temperature prior to pouring an aliquot into the syringe. Remove the plunger from a syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add the surrogate spiking solution (Section 6.7) and internal standard spiking solution (Section 7.3.1.3) through the valve bore, then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. Autosamplers designed for purge-and-trap analysis of volatiles also may be used.

10.4 Attach the syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber.

10.5 Close both valves and purge the sample at a temperature, flow rate, and duration sufficient to purge the less-volatile analytes onto the trap, yet short enough to prevent blowing the more-volatile analytes through the trap. The temperature, flow rate, and time should be determined by test. The same purge temperature, flow rate, and purge time must be used for all calibration, QC, and field samples.

10.6 After the purge, set the purge-and-trap system to the desorb mode (Figure 4), and begin to temperature program the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to the desorb temperature while backflushing the trap with carrier gas at the flow rate and for the time necessary to desorb the analytes of interest. The optimum temperature, flow rate, and time should be determined by test. The

same temperature, desorb time, and flow rate must be used for all calibration, QC, and field samples. If heating of the trap does not result in sharp peaks for the early eluting analytes, the GC column may be used as a secondary trap by cooling to an ambient or subambient temperature. To avoid carry-over and interferences, maintain the trap at the desorb temperature and flow rate until the analytes, interfering compounds, and excess water are desorbed. The optimum conditions should be determined by test.

10.7 Start MS data acquisition at the start of the desorb cycle and stop data collection when the analytes of interest, potentially interfering compounds, and water have eluted (see the footnote to Table 3 for conditions).

10.8 Cool the trap to the purge temperature and return the trap to the purge mode (Figure 3). When the trap is cool, the next sample can be analyzed.

11. Performance Tests

11.1 At the beginning of each 12-hour shift during which analyses are to be performed, GC/MS performance must be verified before blanks or samples may be analyzed (Section 8.4). Use the instrument operating conditions in the footnotes to Table 3 for these performance tests. Alternate conditions may be used so as long as all QC requirements are met.

11.2 BFB—Inject 50 ng of BFB solution directly on the column. Alternatively, add BFB to reagent water or an aqueous standard such that 50 ng or less of BFB will be introduced into the GC. Analyze according to Section 10. Confirm that all criteria in Section 7.3.2.2 and Table 4 are met. If all criteria are not met, perform system repair, retune the mass spectrometer, and repeat the test until all criteria are met.

11.3 GC resolution—There must be a valley between 1,2-dibromoethane and chlorobenzene, and the height of the valley must not exceed 25 percent of the shorter of the two peaks. For an alternate GC column, apply this valley height criterion to two representative GC peaks separated by no more than 7 seconds.

11.4 Verify calibration with the LCS (Section 8.4) after the criteria for BFB are met (Reference 15) and prior to analysis of a blank or sample. After verification, analyze a blank (Section 8.5) to demonstrate freedom from contamination and carry-over at the MDL.

12. Qualitative Identification

12.1 Target analytes are identified by comparison of results from analysis of a sample or blank with data stored in the GC/MS data system (Section 7.3.2.3). Identification of an analyte is confirmed per Sections 12.1.1 through 12.1.4.

12.1.1 The signals for all characteristic m/z's stored in the data system (Section 7.3.2.3) for each analyte of interest must be present and must maximize within the same two consecutive scans.

12.1.2 Based on the relative retention time (RRT), the RRT for the analyte must be within ± 0.06 of the RRT of the analyte in the LCS run at the beginning of the shift (Section 8.4). Relative retention time is used to establish the identification window because it compensates for small changes in the GC temperature program whereas the absolute retention time does not (see Section 7.3.1.2).

Note: RRT is a unitless quantity (see Sec. 20.2), although some procedures refer to ''RRT units'' in providing the specification for the agreement between the RRT values in the sample and the LCS or other standard.

12.1.3 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum, must agree within 50% to 200% (½ to 2 times) for all m/z's in the reference mass spectrum stored in the data system (Section 7.3.2.3), or from a reference library. For example, if a peak has an intensity of 20% relative to the base peak, the analyte is identified if the intensity of the peak in the sample is in the range of 10% to 40% of the base peak.

12.1.4 The m/z's present in the acquired mass spectrum for the sample that are not present in the reference mass spectrum must be accounted for by contaminant or background m/z's. A reference library may be helpful to identify and account for background or contaminant m/z's. If the acquired mass spectrum is contaminated, or if identification is ambiguous, an experienced spectrometrist (Section 1.6) must determine the presence or absence of the compound.

12.2 Structural isomers that have very similar mass spectra can be identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 50% of the height of the shorter of the two peaks. Otherwise, structural isomers are identified as isomeric pairs.

13. Calculations

13.1 When an analyte has been identified, quantitation of that analyte is based on the integrated abundance from the EICP of the primary characteristic m/z in Table 5 or 6. Calculate the concentration using the response factor (RF) determined in Section 7.3.3 and Equation 2. If a calibration curve was used, calculate the concentration using the regression equation for the curve. If the concentration of an analyte exceeds the calibration range, dilute the sample by the minimum amount to bring the concentration into the calibration range, and re-analyze. Determine a dilution factor (DF) from the amount of the dilution. For example, if the extract is diluted by a factor of 2, DF = 2.

$$C_s\ (\mu g/L) = \frac{A_s \times C_{is} \times DF}{A_{is} \times RF}$$

Where:

C_s = Concentration of the analyte in the sample, and the other terms are as defined in Section 7.3.3.

13.2 Reporting of results.

As noted in Section 1.4.1, EPA has promulgated this method at 40 CFR part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described here are focused on such monitoring needs and may not be relevant to other uses of the method.

13.2.1 Report results for wastewater samples in µg/L without correction for recovery. (Other units may be used if required by in a permit.) Report all QC data with the sample results.

13.2.2 Reporting level.

Unless otherwise specified in by a regulatory authority or in a discharge permit, results for analytes that meet the identification criteria are reported down to the concentration of the ML established by the laboratory through calibration of the instrument (see Section 7.3.2 and the glossary for the derivation of the ML). EPA considers the terms ''reporting limit,'' ''quantitation limit,'' and ''minimum level'' to be synonymous.

13.2.2.1 Report a result for each analyte in each sample, blank, or standard at or above the ML to 3 significant figures. Report a result for each analyte found in each sample below the ML as ''<ML,'' or as required by the regulatory authority or permit. Results are reported without blank subtraction unless requested or required by a regulatory authority or in a permit. In this case, both the sample result and the blank results must be reported together.

13.2.2.2 In addition to reporting results for samples and blanks separately, the concentration of each analyte in a blank associated with the

sample may be subtracted from the result for that sample, but only if requested or required by a regulatory authority or in a permit. In this case, both the sample result and the blank results must be reported together.

13.2.2.3 Report a result for an analyte found in a sample that has been diluted at the least dilute level at which the area at the quantitation m/z is within the calibration range (*i.e.,* above the ML for the analyte) and the MS/MSD recovery and RPD are within their respective QC acceptance criteria (Table 7). This may require reporting results for some analytes from different analyses.

13.2.3 Results from tests performed with an analytical system that is not in control (*i.e.,* that does not meet acceptance criteria for all of QC tests in this method) must not be reported or otherwise used for permitting or regulatory compliance purposes, but do not relieve a discharger or permittee of reporting timely results. If the holding time would be exceeded for a re-analysis of the sample, the regulatory/control authority should be consulted for disposition.

14. Method Performance

14.1 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5–600 µg/L (References 4 and 16). Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 8.

14.2 As noted in Sec. 1.1, this method was validated through an interlaboratory study conducted more than 29 years ago. However, the fundamental chemistry principles used in this method remain sound and continue to apply.

15. Pollution Prevention

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operations. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, the laboratory should use pollution prevention techniques to address waste generation. When wastes cannot be reduced at the source, the Agency recommends recycling as the next best option.

15.2 The analytes in this method are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

15.3 For information about pollution prevention that may be applied to laboratories and research institutions, consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW., Washington, DC 20036, 202/872–4477.

16. Waste Management

16.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. An overview of requirements can be found in Environmental Management Guide for Small Laboratories (EPA 233–B–98–001).

16.2 Samples at pH <2, or pH >12, are hazardous and must be neutralized before being poured down a drain, or must be handled and disposed of as hazardous waste.

16.3 Many analytes in this method decompose above 500 °C. Low-level waste such as absorbent paper, tissues, and plastic gloves may be burned in an appropriate incinerator. Gross quantities of neat or highly concentrated solutions of toxic or hazardous chemicals should be packaged securely and disposed of through commercial or governmental channels that are capable of handling these types of wastes.

16.4 For further information on waste management, consult The Waste Management Manual for Laboratory Personnel and Less is Better-Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW., Washington, DC 20036, 202/872–4477.

17. References

1. Bellar, T.A. and Lichtenberg, J.J. ''Determining Volatile Organics at Microgram-per-Litre Levels by Gas Chromatography,'' Journal American Water Works Association, 66, 739 (1974).
2. ''Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants,'' U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1977, Revised April 1977.
3. Bellar, T.A. and Lichtenberg, J.J. ''Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds,'' Measurement of Organic Pollutants in Water and Wastewater, C.E. Van Hall, editor, American Society for Testing and Materials, Philadelphia, PA. Special Technical Publication 686, 1978.
4. ''EPA Method Study 29 EPA Method 624-Purgeables,'' EPA 600/4–84–054, National Technical Information Service, PB84–209915, Springfield, Virginia 22161, June 1984.
5. 40 CFR part 136, appendix B.
6. ''Method Detection Limit for Methods 624 and 625,'' Olynyk, P., Budde, W.L., and Eichelberger, J.W. Unpublished report, May 14, 1980.
7. ''Carcinogens-Working With Carcinogens,'' Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77–206, August 1977.
8. ''OSHA Safety and Health Standards, General Industry,'' (29 CFR part 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).
9. ''Safety in Academic Chemistry Laboratories,'' American Chemical Society Publication, Committee on Chemical Safety, 7th Edition, 2003.
10. 40 CFR 136.6(b)(5)(x).
11. 40 CFR 136.6(b)(2)(i).
12. Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water (EPA–821–B–98–003) March 1999
13. Provost, L.P. and Elder, R.S. ''Interpretation of Percent Recovery Data,'' American Laboratory, 15, 58–63 (1983).
14. 40 CFR 136.3(a), Table IB, Chlorine—Total residual
15. Budde, W.L. and Eichelberger, J.W. ''Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories,'' EPA–600/4–80–025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, April 1980.
16. ''Method Performance Data for Method 624,'' Memorandum from R. Slater and T. Pressley, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, January 17, 1984.

18. Tables

TABLE 1—PURGEABLES [1]

Analyte	CAS Registry No.	MDL (μg/L) [2]	ML (μg/L) [3]
Acrolein	107–02–8		
Acrylonitrile	107–13–1		
Benzene	71–43–2	4.4	13.2
Bromodichloromethane	75–27–4	2.2	6.6
Bromoform	75–25–2	4.7	14.1
Bromomethane	74–83–9		
Carbon tetrachloride	56–23–5	2.8	8.4
Chlorobenzene	108–90–7	6.0	18.0
Chloroethane	75–00–3		
2-Chloroethylvinyl ether	110–75–8		
Chloroform	67–66–3	1.6	4.8
Chloromethane	74–87–3		
Dibromochloromethane	124–48–1	3.1	9.3
1,2-Dichlorobenzene	95–50–1		
1,3-Dichlorobenzene	541–73–1		
1,4-Dichlorobenzene	106–46–7		
1,1-Dichloroethane	75–34–3	4.7	14.1
1,2-Dichloroethane	107–06–2	2.8	8.4
1,1-Dichloroethene	75–35–4	2.8	8.4
trans-1,2-Dichloroethene	156–60–5	1.6	4.8
1,2-Dichloropropane	78–87–5	6.0	18.0
cis-1,3-Dichloropropene	10061–01–5	5.0	15.0
trans-1,3-Dichloropropene	10061–02–6		
Ethyl benzene	100–41–4	7.2	21.6
Methylene chloride	75–09–2	2.8	8.4
1,1,2,2-Tetrachloroethane	79–34–5	6.9	20.7
Tetrachloroethene	127–18–4	4.1	12.3
Toluene	108–88–3	6.0	18.0
1,1,1-Trichloroethane	71–55–6	3.8	11.4
1,1,2-Trichloroethane	79–00–5	5.0	15.0
Trichloroethene	79–01–6	1.9	5.7
Vinyl chloride	75–01–4		

[1] All the analytes in this table are Priority Pollutants (40 CFR part 423, appendix A)
[2] MDL values from the 1984 promulgated version of Method 624
[3] ML = Minimum Level—see Glossary for definition and derivation

TABLE 2—ADDITIONAL PURGEABLES

Analyte	CAS Registry
Acetone [1]	67–64–1
Acetonitrile [2]	75–05–8
Allyl alcohol [1]	107–18–6
Allyl chloride	107–05–1
t-Amyl ethyl ether (TAEE)	919–94–8
t-Amyl methyl ether (TAME)	994–058
Benzyl chloride	100–44–7
Bromoacetone [2]	598–31–2
Bromobenzene	108–86–1
Bromochloromethane	74–97–5
1,3-Butadiene	106–99–0
n-Butanol [1]	71–36–3
2-Butanone (MEK) [1 2]	78–93–3
t-Butyl alcohol (TBA)	75–65–0
n-Butylbenzene	104–51–8
sec-Butylbenzene	135–98–8
t-Butylbenzene	98–06–6
t-Butyl ethyl ether (ETBE)	637–92–3
Carbon disulfide	75–15–0
Chloral hydrate [2]	302–17–0
Chloroacetonitrile [1]	107–14–2
1-Chlorobutane	109–69–3
Chlorodifluoromethane	75–45–6
2-Chloroethanol [2]	107–07–3
bis (2-Chloroethyl) sulfide [2]	505–60–2
1-Chlorohexanone	20261–68–1
Chloroprene (2-chloro-1,3-butadiene)	126–99–8
3-Chloropropene	107–05–1
3-Chloropropionitrile	542–76–7

TABLE 2—ADDITIONAL PURGEABLES—Continued

Analyte	CAS Registry
2-Chlorotoluene	95–49–8
4-Chlorotoluene	106–43–4
Crotonaldehyde [1 2]	123–73–9
Cyclohexanone	108–94–1
1,2-Dibromo-3-chloropropane	96–12–8
1,2-Dibromoethane	106–93–4
Dibromomethane	74–95–3
cis-1,4-Dichloro-2-butene	1476–11–5
trans-1,4-Dichloro-2-butene	110–57–6
cis-1,2-Dichloroethene	156–59–2
Dichlorodifluoromethane	75–71–8
1,3-Dichloropropane	142–28–9
2,2-Dichloropropane	590–20–7
1,3-Dichloro-2-propanol [2]	96–23–1
1,1-Dichloropropene	563–58–6
cis-1,3-Dichloropropene	10061–01–5
1:2,3:4-Diepoxybutane	1464–53–5
Diethyl ether	60–29–7
Diisopropyl ether (DIPE)	108–20–3
1,4-Dioxane [2]	123–91–1
Epichlorohydrin [2]	106–89–8
Ethanol [2]	64–17–5
Ethyl acetate [2]	141–78–6
Ethyl methacrylate	97–63–2
Ethylene oxide [2]	75–21–8
Hexachlorobutadiene	87–63–3
Hexachloroethane	67–72–1
2-Hexanone [2]	591–78–6
Iodomethane	74–88–4
Isobutyl alcohol [1]	78–83–1

TABLE 2—ADDITIONAL PURGEABLES—Continued

Analyte	CAS Registry
Isopropylbenzene	98–82–8
p-Isopropyltoluene	99–87–6
Methacrylonitrile [2]	126–98–7
Methanol [2]	67–56–1
Malonitrile [2]	109–77–3
Methyl acetate	79–20–9
Methyl acrylate	96–33–3
Methyl cyclohexane	108–87–2
Methyl iodide	74–88–4
Methyl methacrylate	78–83–1
4-Methyl-2-pentanone (MIBK) [2]	108–10–1
Methyl-*t*-butyl ether (MTBE)	1634–04–4
Naphthalene	91–20–3
Nitrobenzene	98–95–3
N-Nitroso-di-*n*-butylamine [2]	924–16–3
2-Nitropropane	79–46–9
Paraldehyde [2]	123–63–7
Pentachloroethane [2]	76–01–7
Pentafluorobenzene	363–72–4
2-Pentanone [2]	107–19–7
2-Picoline [2]	109–06–8
1-Propanol [1]	71–23–8
2-Propanol [1]	67–63–0
Propargyl alcohol [2]	107–19–7
beta-Propiolactone [2]	57–58–8
Propionitrile (ethyl cyanide) [1]	107–12–0
n-Propylamine	107–10–8
n-Propylbenzene	103–65–1
Pyridine [2]	110–86–1

TABLE 2—ADDITIONAL PURGEABLES—Continued

Analyte	CAS Registry
Styrene	100–42–5
1,1,1,2-Tetrachloroethane	630–20–6
Tetrahydrofuran	109–99–9
o-Toluidine [2]	95–53–4
1,2,3-Trichlorobenzene	87–61–6
Trichlorofluoromethane	75–69–4
1,2,3-Trichloropropane	96–18–4
1,2,3-Trimethylbenzene	526–73–8
1,2,4-Trimethylbenzene	95–63–6
1,3,5-Trimethylbenzene	108–67–8
Vinyl acetate	108–05–4
m-Xylene [3]	108–38–3
o-Xylene [3]	95–47–6
p-Xylene [3]	106–42–3
m+o- Xylene [3]	179601–22–0
m+p- Xylene [3]	179601–23–1
o+p- Xylene [3]	136777–61–2

[1] Determined at a purge temperature of 80 °C.
[2] May be detectable at a purge temperature of 80 °C.
[3] Determined in combination separated by GC column. Most GC columns will resolve *o*-xylene from *m+p*-xylene. Report using the CAS number for the individual xylene or the combination, as determined.

TABLE 3—EXAMPLE RETENTION TIMES

Analyte	Retention time (min)
Chloromethane	3.68
Vinyl chloride	3.92
Bromomethane	4.50
Chloroethane	4.65
Trichlorofluoromethane	5.25
Diethyl ether	5.88
Acrolein	6.12
1,1-Dichloroethene	6.30
Acetone	6.40

TABLE 3—EXAMPLE RETENTION TIMES—Continued

Analyte	Retention time (min)
Iodomethane	6.58
Carbon disulfide	6.72
3-Chloropropene	6.98
Methylene chloride	7.22
Acrylonitrile	7.63
trans-1,2-Dichloroethene	7.73
1,1-Dichloroethane	8.45
Vinyl acetate	8.55
Allyl alcohol	8.58
2-Chloro-1,3-butadiene	8.65
Methyl ethyl ketone	9.50
cis-1,2-Dichloroethene	9.50
Ethyl cyanide	9.57
Methacrylonitrile	9.83
Chloroform	10.05
1,1,1-Trichloroethane	10.37
Carbon tetrachloride	10.70
Isobutanol	10.77
Benzene	10.98
1,2-Dichloroethane	11.00
Crotonaldehyde	11.45
Trichloroethene	12.08
1,2-Dichloropropane	12.37
Methyl methacrylate	12.55
p-Dioxane	12.63
Dibromomethane	12.65
Bromodichloromethane	12.95
Chloroacetonitrile	13.27
2-Chloroethylvinyl ether	13.45
cis-1,3-Dichloropropene	13.65
4-Methyl-2-pentanone	13.83
Toluene	14.18
trans-1,3-Dichloropropene	14.57
Ethyl methacrylate	14.70
1,1,2-Trichloroethane	14.93
1,3-Dichloropropane	15.18
Tetrachloroethene	15.22
2-Hexanone	15.30
Dibromochloromethane	15.68
1,2-Dibromoethane	15.90

TABLE 3—EXAMPLE RETENTION TIMES—Continued

Analyte	Retention time (min)
Chlorobenzene	16.78
Ethylbenzene	16.82
1,1,1,2-Tetrachloroethane	16.87
m+p-Xylene	17.08
o-Xylene	17.82
Bromoform	18.27
Bromofluorobenzene	18.80
1,1,2,2-Tetrachloroethane	18.98
1,2,3-Trichloropropane	19.08
trans-1,4-Dichloro-2-butene	19.12

Column: 75 m x 0.53 mm ID x 3.0 μm wide-bore DB–624.
Conditions: 40°C for 4 min, 9°C/min to 200°C, 20°C/min (or higher) to 250°C, hold for 20 min at 250°C to remove water.
Carrier gas flow rate: 6–7 mL/min at 40°C.
Inlet split ratio: 3:1.
Interface split ratio: 7:2.

TABLE 4—BFB KEY M/Z ABUNDANCE CRITERIA [1]

m/z	Abundance criteria
50	15–40% of m/z 95.
75	30–60% of m/z 95.
95	Base Peak, 100% Relative Abundance.
96	5–9% of m/z 95.
173	<2% of m/z 174.
174	>50% of m/z 95.
175	5–9% of m/z 174.
176	>95% but <101% of m/z 174.
177	5–9% of m/z 176.

[1] Abundance criteria are for a quadrupole mass spectrometer; contact the manufacturer for criteria for other types of mass spectrometers.

TABLE 5—SUGGESTED SURROGATE AND INTERNAL STANDARDS

Analyte	Retention time (min) [1]	Primary m/z	Secondary m/z's
Benzene-d_6	10.95	84	
4-Bromofluorobenzene	18.80	95	174, 176
Bromochloromethane	9.88	128	49, 130, 51
2-Bromo-1-chloropropane	14.80	77	79, 156
2-Butanone-d_5	9.33	77	
Chloroethane-d_5	4.63	71	
Chloroform-^{13}C	10.00	86	
1,2-Dichlorobenzene-d_4		152	
1,4-Dichlorobutane	18.57	55	90, 92
1,2-Dichloroethane-d_4	10.88	102	
1,1-Dichloroethene-d_2	6.30	65	
1,2-Dichloropropane-d_6	12.27	67	
trans-1,3-Dichloropropene-d_4	14.50	79	
1,4-Difluorobenzene		114	63, 88
Ethylbenzene-d_{10}	16.77	98	
Fluorobenzene		96	70
2-Hexanone-d_5	15.30	63	
Pentafluorobenzene		168	
1,1,2,2-Tetrachloroethane-d_2	18.93	84	
Toluene-d_8	14.13	100	
Vinyl chloride-d_3	3.87	65	

[1] For chromatographic conditions, see the footnote to Table 3.

TABLE 6—CHARACTERISTIC M/Z'S FOR PURGEABLE ORGANICS

Analyte	Primary m/z	Secondary m/z's
Chloromethane	50	52.
Bromomethane	94	96.
Vinyl chloride	62	64.
Chloroethane	64	66.
Methylene chloride	84	49, 51, and 86.
Trichlorofluoromethane	101	103.
1,1-Dichloroethene	96	61 and 98.
1,1-Dichloroethane	63	65, 83, 85, 98, and 100.
trans-1,2-Dichloroethene	96	61 and 98.
Chloroform	83	85.
1,2-Dichloroethane	98	62, 64, and 100.
1,1,1-Trichloroethane	97	99, 117, and 119.
Carbon tetrachloride	117	119 and 121.
Bromodichloromethane	83	127, 85, and 129.
1,2-Dichloropropane	63	112, 65, and 114.
trans-1,3-Dichloropropene	75	77.
Trichloroethene	130	95, 97, and 132.
Benzene	78	
Dibromochloromethane	127	129, 208, and 206.
1,1,2-Trichloroethane	97	83, 85, 99, 132, and 134.
cis-1,3-Dichloropropene	75	77.
2-Chloroethylvinyl ether	106	63 and 65.
Bromoform	173	171, 175, 250, 252, 254, and 256.
1,1,2,2-Tetrachloroethane	168	83, 85, 131, 133, and 166.
Tetrachloroethene	164	129, 131, and 166.
Toluene	92	91.
Chlorobenzene	112	114.
Ethyl benzene	106	91.
1,3-Dichlorobenzene	146	148 and 111.
1,2-Dichlorobenzene	146	148 and 111.
1,4-Dichlorobenzene	146	148 and 111.

TABLE 7—LCS (Q), DOC (S AND $\overline{X}$), AND MS/MSD (P AND RPD) ACCEPTANCE CRITERIA [1]

Analyte	Range for Q (%)	Limit for s (%)	Range for $\overline{X}$ (%)	Range for P (%)	Limit for RPD
Benzene	65–135	33	75–125	37–151	61
Benzene-d_6				70–130	
Bromodichloromethane	65–135	34	50–140	35–155	56
Bromoform	70–130	25	57–156	45–169	42
Bromomethane	15–185	90	D–206	D–242	61
2-Butanone-d_5				60–140	
Carbon tetrachloride	70–130	26	65–125	70–140	41
Chlorobenzene	65–135	29	82–137	37–160	53
Chloroethane	40–160	47	42–202	14–230	78
Chloroethane-d_5				60–140	
2-Chloroethylvinyl ether	D–225	130	D–252	D–305	71
Chloroform	70–135	32	68–121	51–138	54
Chloroform-^{13}C				70–130	
Chloromethane	D–205	472	D–230	D–273	60
Dibromochloromethane	70–135	30	69–133	53–149	50
1,2-Dichlorobenzene	65–135	31	59–174	18–190	57
1,2-Dichlorobenzene-d_4				70–130	
1,3-Dichlorobenzene	70–130	24	75–144	59–156	43
1,4-Dichlorobenzene	65–135	31	59–174	18–190	57
1,1-Dichloroethane	70–130	24	71–143	59–155	40
1,2-Dichloroethane	70–130	29	72–137	49–155	49
1,2-Dichloroethane-d_4				70–130	
1,1-Dichloroethene	50–150	40	19–212	D–234	32
1,1-Dichloroethene-d_2				70–130	
trans-1,2-Dichloroethene	70–130	27	68–143	54–156	45
1,2-Dichloropropane	35–165	69	19–181	D–210	55
1,2-Dichloropropane-d_6				60–140	
cis-1,3-Dichloropropene	25–175	79	5–195	D–227	58
trans-1,3-Dichloropropene	50–150	52	38–162	17–183	86
trans-1,3-Dichloropropene-d_4				70–130	
Ethyl benzene	60–140	34	75–134	37–162	63
2-Hexanone-d_5				60–140	
Methylene chloride	60–140	192	D–205	D–221	28
1,1,2,2-Tetrachloroethane	60–140	36	68–136	46–157	61
1,1,2,2-Tetrachloroethane-d_2				70–130	
Tetrachloroethene	70–130	23	65–133	64–148	39

TABLE 7—LCS (Q), DOC (S AND $\bar{X}$), AND MS/MSD (P AND RPD) ACCEPTANCE CRITERIA [1]—Continued

Analyte	Range for Q (%)	Limit for s (%)	Range for $\bar{X}$ (%)	Range for P (%)	Limit for RPD
Toluene	70–130	22	75–134	47–150	41
Toluene-d_8	.....	.....	.....	70–130	.....
1,1,1-Trichloroethane	70–130	21	69–151	52–162	36
1,1,2-Trichloroethane	70–130	27	75–136	52–150	45
Trichloroethene	65–135	29	75–138	70–157	48
Trichlorofluoromethane	50–150	50	45–158	17–181	84
Vinyl chloride	5–195	100	D–218	D–251	66
Vinyl chloride-d_3	.....	.....	.....	70–130	.....

[1] Criteria were calculated using an LCS concentration of 20 μg/L
Q = Percent recovery in calibration verification/LCS (Section 8.4)
s = Standard deviation of percent recovery for four recovery measurements (Section 8.2.4)
$\bar{X}$ = Average percent recovery for four recovery measurements (Section 8.2.4)
P = Percent recovery for the MS or MSD (Section 8.3.3)
D = Detected; result must be greater than zero
Notes:
1. Criteria for pollutants are based upon the method performance data in Reference 4. Where necessary, limits for recovery have been broadened to assure applicability to concentrations below those used to develop Table 7.
2. Criteria for surrogates are from EPA CLP SOM01.2D.

TABLE 8—RECOVERY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Analyte	Recovery, X′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
Benzene	0.93C+2.00	20.26 $\bar{X}$ − 1.74	0.25 $\bar{X}$ − 1.33
Bromodichloromethane	1.03C − 1.58	0.15 $\bar{X}$+0.59	0.20 $\bar{X}$+1.13
Bromoform	1.18C − 2.35	0.12 $\bar{X}$+0.36	0.17 $\bar{X}$+1.38
Bromomethane [a]	1.00C	0.43 $\bar{X}$	0.58 $\bar{X}$
Carbon tetrachloride	1.10C − 1.68	0.12 $\bar{X}$+0.25	0.11 $\bar{X}$+0.37
Chlorobenzene	0.98C+2.28	0.16 $\bar{X}$ − 0.09	0.26 $\bar{X}$ − 1.92
Chloroethane	1.18C+0.81	0.14 $\bar{X}$+2.78	0.29 $\bar{X}$+1.75
2-Chloroethylvinyl ether [a]	1.00C	0.62 $\bar{X}$	0.84 $\bar{X}$
Chloroform	0.93C+0.33	0.16 $\bar{X}$+0.22	0.18 $\bar{X}$+0.16
Chloromethane	1.03C+0.81	0.37 $\bar{X}$+2.14	0.58 $\bar{X}$+0.43
Dibromochloromethane	1.01C − 0.03	0.17 $\bar{X}$ − 0.18	0.17 $\bar{X}$+0.49
1,2-Dichlorobenzene [b]	0.94C+4.47	0.22 $\bar{X}$ − 1.45	0.30 $\bar{X}$ − 1.20
1,3-Dichlorobenzene	1.06C+1.68	0.14 $\bar{X}$ − 0.48	0.18 $\bar{X}$ − 0.82
1,4-Dichlorobenzene [b]	0.94C+4.47	0.22 $\bar{X}$ − 1.45	0.30 $\bar{X}$ − 1.20
1,1-Dichloroethane	1.05C+0.36	0.13 $\bar{X}$ − 0.05	0.16 $\bar{X}$+0.47
1,2-Dichloroethane	1.02C+0.45	0.17 $\bar{X}$ − 0.32	0.21 $\bar{X}$ − 0.38
1,1-Dichloroethene	1.12C+0.61	0.17 $\bar{X}$+1.06	0.43 $\bar{X}$ − 0.22
trans-1,2,-Dichloroethene	1.05C+0.03	0.14 $\bar{X}$+0.09	0.19 $\bar{X}$+0.17
1,2-Dichloropropane [a]	1.00C	0.33 $\bar{X}$	0.45 $\bar{X}$
cis-1,3-Dichloropropene [a]	1.00C	0.38 $\bar{X}$	0.52 $\bar{X}$
trans-1,3-Dichloropropene [a]	1.00C	0.25 $\bar{X}$	0.34 $\bar{X}$
Ethyl benzene	0.98C+2.48	0.14 $\bar{X}$+1.00	0.26 $\bar{X}$ − 1.72
Methylene chloride	0.87C+1.88	0.15 $\bar{X}$+1.07	0.32 $\bar{X}$+4.00
1,1,2,2-Tetrachloroethane	0.93C+1.76	0.16 $\bar{X}$+0.69	0.20 $\bar{X}$+0.41
Tetrachloroethene	1.06C+0.60	0.13 $\bar{X}$ − 0.18	0.16 $\bar{X}$ − 0.45
Toluene	0.98C+2.03	0.15 $\bar{X}$ − 0.71	0.22 $\bar{X}$ − 1.71
1,1,1-Trichloroethane	1.06C+0.73	0.12 $\bar{X}$ − 0.15	0.21 $\bar{X}$ − 0.39
1,1,2-Trichloroethane	0.95C+1.71	0.14 $\bar{X}$+0.02	0.18 $\bar{X}$+0.00
Trichloroethene	1.04C+2.27	0.13 $\bar{X}$+0.36	0.12 $\bar{X}$+0.59
Trichlorofluoromethane	0.99C+0.39	0.33 $\bar{X}$ − 1.48	0.34 $\bar{X}$ − 0.39
Vinyl chloride	1.00C	0.48 $\bar{X}$	0.65 $\bar{X}$

X′ = Expected recovery for one or more measurements of a sample containing a concentration of C, in μg/L.
S_r' = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in μg/L.
S′ = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in μg/L.
C = True value for the concentration, in μg/L.
X = Average recovery found for measurements of samples containing a concentration of C, in μg/L.
[a] Estimates based upon the performance in a single laboratory (References 4 and 16).
[b] Due to coelutions, performance statements for these isomers are based upon the sums of their concentrations.

19. Figures

BILLING CODE 6560–50–P

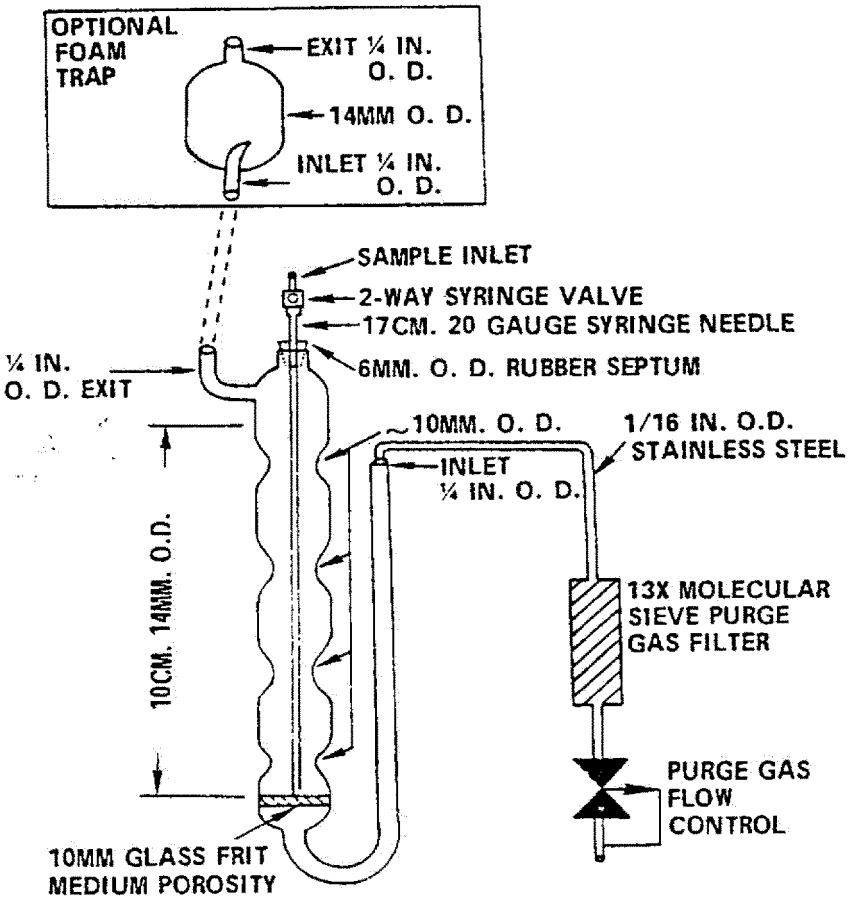


Figure 1. Purging device.

BILLING CODE 6560–50–C

20. Glossary

These definitions and purposes are specific to this method, but have been conformed to common usage to the extent possible.

20.1 Units of weight and measure and their abbreviations

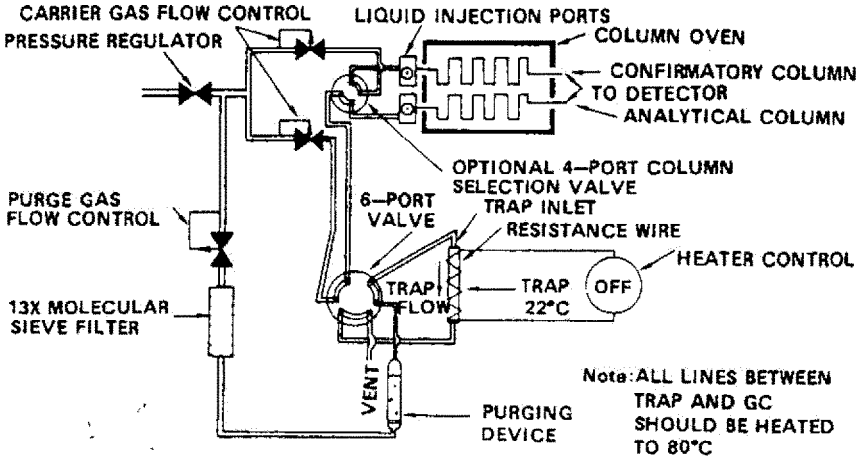


Figure 3. Purge and trap system - purge mode.

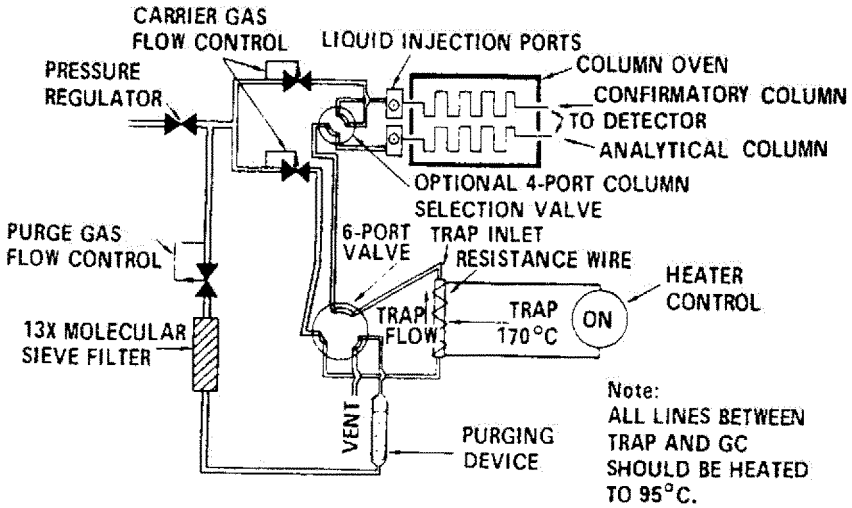


Figure 4. Purge and trap system - desorb mode.

20.1.1 Symbols

°C degrees Celsius
µg microgram
µL microliter
< less than
> greater than
% percent

20.1.2 Abbreviations (in alphabetical order)

cm centimeter
g gram
h hour
ID inside diameter
in. inch
L liter
M Molecular ion
m mass
mg milligram
min minute
mL milliliter
mm millimeter
ms millisecond
m/z mass-to-charge ratio
N normal; gram molecular weight of solute divided by hydrogen equivalent of solute, per liter of solution
ng nanogram
pg picogram
ppb part-per-billion
ppm part-per-million
ppt part-per-trillion
psig pounds-per-square inch gauge
v/v volume per unit volume
w/v weight per unit volume

20.2 Definitions and acronyms (in alphabetical order)

Analyte—A compound tested for by this method. The analytes are listed in Tables 1 and 2.

Analyte of interest—An analyte of interest is an analyte required to be

determined by a regulatory/control authority or in a permit, or by a client.

Analytical batch—The set of samples analyzed on a given instrument during a 12-hour period that begins and ends with analysis of a calibration verification/LCS. See Section 8.4.

Blank—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus. See Section 8.5.

Calibration—The process of determining the relationship between the output or response of a measuring instrument and the value of an input standard. Historically, EPA has referred to a multi-point calibration as the ''initial calibration,'' to differentiate it from a single-point calibration verification.

Calibration standard—A solution prepared from stock solutions and/or a secondary standards and containing the analytes of interest, surrogates, and internal standards. The calibration standard is used to calibrate the response of the GC/MS instrument against analyte concentration.

Calibration verification standard—The laboratory control sample (LCS) used to verify calibration. See Section 8.4.

Descriptor—In SIM, the beginning and ending retention times for the RT window, the m/z's sampled in the RT window, and the dwell time at each m/z.

Extracted ion current profile (EICP)—The line described by the signal at a given m/z.

Field duplicates—Two samples collected at the same time and place under identical conditions, and treated identically throughout field and laboratory procedures. Results of analyses of field duplicates provide an estimate of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

Field blank—An aliquot of reagent water or other reference matrix that is placed in a sample container in the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

GC—Gas chromatograph or gas chromatography

Internal standard—A compound added to a sample in a known amount and used as a reference for quantitation of the analytes of interest and surrogates. Internal standards are listed in Table 5. Also see Internal standard quantitation.

Internal standard quantitation—A means of determining the concentration of an analyte of interest (Tables 1 and 2) by reference to a compound added to a sample and not expected to be found in the sample.

DOC—Initial demonstration of capability (DOC; Section 8.2); four aliquots of reagent water spiked with the analytes of interest and analyzed to establish the ability of the laboratory to generate acceptable precision and recovery. A DOC is performed prior to the first time this method is used and any time the method or instrumentation is modified.

Laboratory control sample (LCS; laboratory fortified blank (LFB); on-going precision and recovery sample; OPR)—An aliquot of reagent water spiked with known quantities of the analytes of interest and surrogates. The LCS is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery. In this method, the LCS is synonymous with a calibration verification sample (See Sections 7.4 and 8.4).

Laboratory fortified sample matrix—See Matrix spike.

Laboratory reagent blank—See Blank.

Matrix spike (MS) and matrix spike duplicate (MSD) (laboratory fortified sample matrix and duplicate)—Two aliquots of an environmental sample to which known quantities of the analytes of interest and surrogates are added in the laboratory. The MS/MSD are prepared and analyzed exactly like a field sample. Their purpose is to quantify any additional bias and imprecision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations.

May—This action, activity, or procedural step is neither required nor prohibited.

May not—This action, activity, or procedural step is prohibited.

Method blank (laboratory reagent blank)—See Blank.

Method detection limit (MDL)—A detection limit determined by the procedure at 40 CFR part 136, appendix B. The MDLs determined by EPA in the original version of the method are listed in Table 1. As noted in Sec. 1.4, use the MDLs in Table 1 in conjunction with current MDL data from the laboratory actually analyzing samples to assess the sensitivity of this procedure relative to project objectives and regulatory requirements (where applicable).

Minimum level (ML)—The term ''minimum level'' refers to either the sample concentration equivalent to the lowest calibration point in a method or a multiple of the method detection limit (MDL), whichever is higher. Minimum levels may be obtained in several ways: They may be published in a method; they may be based on the lowest acceptable calibration point used by a laboratory; or they may be calculated by multiplying the MDL in a method, or the MDL determined by a laboratory, by a factor of 3. For the purposes of NPDES compliance monitoring, EPA considers the following terms to be synonymous: ''quantitation limit,'' ''reporting limit,'' and ''minimum level.''

MS—Mass spectrometer or mass spectrometry.

Must—This action, activity, or procedural step is required.

m/z—The ratio of the mass of an ion (m) detected in the mass spectrometer to the charge (z) of that ion.

Quality control sample (QCS)—A sample containing analytes of interest at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards.

The purpose is to check laboratory performance using test materials that have been prepared independent of the normal preparation process.

Reagent water—Water demonstrated to be free from the analytes of interest and potentially interfering substances at the MDLs for the analytes in this method.

Regulatory compliance limit (or regulatory concentration limit)—A limit on the concentration or amount of a pollutant or contaminant specified in a nationwide standard, in a permit, or otherwise established by a regulatory/control authority.

Relative retention time (RRT)—The ratio of the retention time of an analyte to the retention time of its associated internal standard. RRT compensates for small changes in the GC temperature program that can affect the absolute retention times of the analyte and internal standard. RRT is a unitless quantity.

Relative standard deviation (RSD)—The standard deviation times 100

divided by the mean. Also termed ''coefficient of variation.''

RF—Response factor. See Section 7.3.3.

RSD—See relative standard deviation.

Safety Data Sheet (SDS)—Written information on a chemical's toxicity, health hazards, physical properties, fire, and reactivity, including storage, spill, and handling precautions that meet the requirements of OSHA, 29 CFR 1910.1200(g) and appendix D to § 1910.1200. United Nations Globally Harmonized System of Classification and Labelling of Chemicals (GHS), third revised edition, United Nations, 2009.

Selected Ion Monitoring (SIM)—An MS technique in which a few m/z's are monitored. When used with gas chromatography, the m/z's monitored are usually changed periodically throughout the chromatographic run to correlate with the characteristic m/z's for the analytes, surrogates, and internal standards as they elute from the chromatographic column. The technique is often used to increase sensitivity and minimize interferences.

Signal-to-noise ratio (S/N)—The height of the signal as measured from the mean (average) of the noise to the peak maximum divided by the width of the noise.

SIM—See Selection Ion Monitoring.

Should—This action, activity, or procedural step is suggested but not required.

Stock solution—A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

Surrogate—A compound unlikely to be found in a sample, and which is spiked into sample in a known amount before purge-and-trap. The surrogate is quantitated with the same procedures used to quantitate the analytes of interest. The purpose of the surrogate is to monitor method performance with each sample.

* * * * *

Method 625.1—Base/Neutrals and Acids by GC/MS

1. Scope and Application

1.1 This method is for determination of semivolatile organic pollutants in industrial discharges and other environmental samples by gas chromatography combined with mass spectrometry (GC/MS), as provided under 40 CFR 136.1. This revision is based on a previous protocol (Reference 1), on the basic revision promulgated October 26, 1984 (49 FR 43234), and on an interlaboratory method validation study (Reference 2). Although this method was validated through an interlaboratory study conducted more than 29 years ago, the fundamental chemistry principles used in this method remain sound and continue to apply.

1.2 The analytes that may be qualitatively and quantitatively determined using this method and their CAS Registry numbers are listed in Tables 1 and 2. The method may be extended to determine the analytes listed in Table 3; however, extraction or gas chromatography of some of these analytes may make quantitative determination difficult. For examples, benzidine is subject to oxidative losses during solvent concentration. Under the alkaline conditions of the extraction, *alpha*-BHC, *gamma*-BHC, endosulfan I and II, and endrin are subject to decomposition. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodiphenylamine and other nitrosoamines may decompose in the gas chromatographic inlet. EPA has provided other methods (*e.g.,* Method 607—Nitrosamines) for determination of some of these analytes.

1.3 The large number of analytes in Tables 1–3 of this method makes testing difficult if all analytes are determined simultaneously. Therefore, it is necessary to determine and perform quality control (QC) tests for the ''analytes of interest'' only. Analytes of interest are those required to be determined by a regulatory/control authority or in a permit, or by a client. If a list of analytes is not specified, the analytes in Tables 1 and 2 must be determined, at a minimum, and QC testing must be performed for these analytes. The analytes in Tables 1 and 2, and some of the analytes in Table 3 have been identified as Toxic Pollutants (40 CFR 401.15), expanded to a list of Priority Pollutants (40 CFR part 423, appendix A).

1.4 In this revision to Method 625, the pesticides and polychlorinated biphenyls (PCBs) have been moved from Table 1 to Table 3 (Additional Analytes) to distinguish these analytes from the analytes required in quality control tests (Tables 1 and 2). QC acceptance criteria for pesticides and PCBs have been retained in Table 6 and may continue to be applied if desired, or if requested or required by a regulatory/control authority or in a permit. Method 608 should be used for determination of pesticides and PCBs. Method 1668C may be useful for determination of PCBs as individual chlorinated biphenyl congeners, and Method 1699 may be useful for determination of pesticides. At the time of writing of this revision, Methods 1668C and 1699 had not been approved for use at 40 CFR part 136. The screening procedure for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8–TCDD) contained in the version of Method 625 promulgated October 26, 1984 (49 FR 43234) has been replaced with procedures for selected ion monitoring (SIM), and 2,3,7,8–TCDD may be determined using the SIM procedures. However, EPA Method 613 or 1613B should be used for analyte-specific determination of 2,3,7,8–TCDD because of the focus of these methods on this compound. Methods 613 and 1613B are approved for use at 40 CFR part 136.

1.5 Method detection limits (MDLs; Reference 3) for the analytes in Tables 1, 2, and 3 are listed in those tables. These MDLs were determined in reagent water (Reference 4). Advances in analytical technology, particularly the use of capillary (open-tubular) columns, allowed laboratories to routinely achieve MDLs for the analytes in this method that are 2–10 times lower than those in the version promulgated in 1984 (40 FR 43234). The MDL for an analyte in a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5.1 EPA has promulgated this method at 40 CFR part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described in Section 15.2 are focused on such monitoring needs and may not be relevant to other uses of the method.

1.5.2 This method includes ''reporting limits'' based on EPA's ''minimum level'' (ML) concept (see the glossary in Section 22). Tables 1, 2, and 3 contain MDL values and ML values for many of the analytes. The MDL for an analyte in a specific wastewater may differ from those listed in Tables 1, 2, and 3, depending upon the nature of interferences in the sample matrix.

1.6 This method is performance-based. It may be modified to improve performance (*e.g.,* to overcome interferences or improve the accuracy of results) provided all performance requirements are met.

1.6.1 Examples of allowed method modifications are described at 40 CFR 136.6. Other examples of allowed modifications specific to this method are described in Section 8.1.2.

1.6.2 Any modification beyond those expressly permitted at 40 CFR 136.6 or in Section 8.1.2 of this method shall be considered a major modification subject to application and approval of an alternate test procedure under 40 CFR 136.4 and 136.5.

1.6.3 For regulatory compliance, any modification must be demonstrated to produce results equivalent or superior to results produced by this method when applied to relevant wastewaters (Section 8.3).

1.7 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 8.2.

1.8 Terms and units of measure used in this method are given in the glossary at the end of the method.

2. Summary of Method

2.1 A measured volume of sample, sufficient to meet an MDL or reporting limit, is serially extracted with methylene chloride at pH 11–13 and again at a pH less than 2 using a separatory funnel or continuous liquid/liquid extractor.

2.2 The extract is concentrated to a volume necessary to meet the required compliance or detection limit, and analyzed by GC/MS. Qualitative identification of an analyte in the extract is performed using the retention time and the relative abundance of two or more characteristic masses (m/z's). Quantitative analysis is performed using the internal standard technique with a single characteristic m/z.

3. Contamination and Interferences

3.1 Solvents, reagents, glassware, and other sample processing labware may yield artifacts, elevated baselines, or matrix interferences causing misinterpretation of chromatograms and mass spectra. All materials used in the analysis must be demonstrated to be free from contamination and interferences by analyzing blanks initially and with each extraction batch (samples started through the extraction process in a given 12-hour period, to a maximum of 20 samples—see Glossary for detailed definition), as described in Section 8.5. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, labware is cleaned by extraction or solvent rinse, or baking in a kiln or oven.

3.2 Glassware must be scrupulously cleaned (Reference 5). Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and reagent water. The glassware should then be drained dry, and heated at 400 °C for 15–30 minutes. Some thermally stable materials, such as PCBs, may require higher temperatures and longer baking times for removal. Solvent rinses with pesticide quality acetone, hexane, or other solvents may be substituted for heating. Volumetric labware should not be heated above 90 °C. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with solvent-rinsed or baked aluminum foil.

3.3 Matrix interferences may be caused by contaminants co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. Interferences extracted from samples high in total organic carbon (TOC) may result in elevated baselines, or by enhancing or suppressing a signal at or near the retention time of an analyte of interest. Analyses of the matrix spike and duplicate (Section 8.3) may be useful in identifying matrix interferences, and gel permeation chromatography (GPC; Section 11.1) and sulfur removal (Section 11.2) may aid in eliminating these interferences. EPA has provided guidance that may aid in overcoming matrix interferences (Reference 6).

3.4 In samples that contain an inordinate number of interferences, the use of chemical ionization (CI) mass spectrometry may make identification easier. Tables 4 and 5 give characteristic CI m/z's for many of the analytes covered by this method. The use of CI mass spectrometry to support electron ionization (EI) mass spectrometry is encouraged, but not required.

4. Safety

4.1 Hazards associated with each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of safety data sheets (SDSs, OSHA, 29 CFR 1910.1200(g)) should also be made available to all personnel involved in sample handling and chemical analysis. Additional references to laboratory safety are available and have been identified (References 7–9) for the information of the analyst.

4.2 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, *alpha*-BHC, *beta*-BHC, *delta*-BHC, *gamma*-BHC, Dibenz(a,h)-anthracene, N-nitrosodimethylamine, 4,4'-DDT, and PCBs. Other compounds in Table 3 may also be toxic. Primary standards of toxic compounds should be prepared in a chemical fume hood, and a NIOSH/MESA approved toxic gas respirator should be worn when handling high concentrations of these compounds.

4.3 This method allows the use of hydrogen as a carrier gas in place of helium (Section 5.6.1.2). The laboratory should take the necessary precautions in dealing with hydrogen, and should limit hydrogen flow at the source to prevent buildup of an explosive mixture of hydrogen in air.

5. Apparatus and Materials

Note: Brand names, suppliers, and part numbers are for illustration purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here. Demonstrating that the equipment and supplies used in the laboratory achieves the required performance is the responsibility of the laboratory. Suppliers for equipment and materials in this method may be found through an on-line search. Please do not contact EPA for supplier information.

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—amber glass bottle large enough to contain the necessary sample volume, fitted with a fluoropolymer-lined screw cap. Foil may be substituted for fluoropolymer if the sample is not corrosive. If amber bottles are not available, protect samples from light. Unless pre-cleaned, the bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—the sampler must incorporate a pre-cleaned glass sample container. Samples must be kept refrigerated at <6 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use,

however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with reagent water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow-proportioned composites.

5.2 Glassware.

5.2.1 Separatory funnel—Size appropriate to hold sample volume and extraction solvent volume, and equipped with fluoropolymer stopcock.

5.2.2 Drying column—Chromatographic column, approximately 400 mm long by 19 mm ID, with coarse frit, or equivalent, sufficient to hold 15 g of anhydrous sodium sulfate.

5.2.3 Concentrator tube, Kuderna-Danish—10 mL, graduated (Kontes 570050–1025 or equivalent). Calibration must be checked at the volumes employed in the test. A ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish—500 mL (Kontes 57001–0500 or equivalent). Attach to concentrator tube with springs.

Note: Use of a solvent recovery system with the K–D or other solvent evaporation apparatus is strongly recommended.

5.2.5 Snyder column, Kuderna-Danish—Three ball macro (Kontes 503000–0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish—Two-ball micro (Kontes 569001–0219 or equivalent).

5.2.7 Vials—10–15 mL, amber glass, with Teflon-lined screw cap.

5.2.8 Continuous liquid-liquid extractor—Equipped with fluoropolymer or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, N.J., P/N 6848–20, or equivalent.)

5.2.9 In addition to the glassware listed above, the laboratory should be equipped with all necessary pipets, volumetric flasks, beakers, and other glassware listed in this method and necessary to perform analyses successfully.

5.3 Boiling chips—Approximately 10/40 mesh, glass, silicon carbide, or equivalent. Heat to 400 °C for 30 minutes, or solvent rinse or Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (±2 °C). The bath should be used in a hood.

5.5 Balances.

5.5.1 Analytical, capable of accurately weighing 0.1 mg.

5.5.2 Top loading, capable of accurately weighing 10 mg.

5.6 GC/MS system.

5.6.1 Gas chromatograph (GC)—An analytical system complete with a temperature programmable gas chromatograph and all required accessories, including syringes and analytical columns.

5.6.1.1 Injection port—Can be split, splitless, temperature programmable split/splitless (PTV), solvent-purge, large-volume, on-column, backflushed, or other. An autosampler is highly recommended because it injects volumes more precisely than volumes injected manually.

5.6.1.2 Carrier gas—Helium or hydrogen. Data in the tables in this method were obtained using helium carrier gas. If hydrogen is used, analytical conditions may need to be adjusted for optimum performance, and calibration and all QC tests must be performed with hydrogen carrier gas. See Section 4.3 for precautions regarding the use of hydrogen as a carrier gas.

5.6.2 GC column—See the footnotes to Tables 4 and 5. Other columns or column systems may be used provided all requirements in this method are met.

5.6.3 Mass spectrometer—Capable of repetitively scanning from 35–450 Daltons (amu) every two seconds or less, utilizing a 70 eV (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 9A or 9B when 50 ng or less of decafluorotriphenyl phosphine (DFTPP; CAS 5074–71–5; bis(pentafluorophenyl) phenyl phosphine) is injected into the GC.

5.6.4 GC/MS interface—Any GC to MS interface that meets all performance requirements in this method may be used.

5.6.5 Data system—A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage of mass spectra acquired throughout the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific m/z's (masses) and plotting m/z abundances versus time or scan number. This type of plot is defined as an extracted ion current profile (EICP). Software must also be available that allows integrating the abundance at any EICP between specified time or scan number limits.

5.7 Automated gel permeation chromatograph (GPC).

5.7.1 GPC column—150—700 mm long x 21–25 mm ID, packed with 70 g of SX–3 Biobeads; Bio-Rad Labs, or equivalent

5.7.2 Pump, injection valve, UV detector, and other apparatus necessary to meet the requirements in this method.

5.8 Nitrogen evaporation device—Equipped with a water bath than can be maintained at 30–45 °C; N-Evap, Organomation Associates, or equivalent.

6. Reagents

6.1 Reagent water—Reagent water is defined as water in which the analytes of interest and interfering compounds are not detected at the MDLs of the analytes of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—(ACS) granular.

6.4 Sulfuric acid (1+1)—Slowly add 50 mL of H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, methanol, methylene chloride, 2-propanol—High purity pesticide quality, or equivalent, demonstrated to be free of the analytes of interest and interferences (Section 3). Purification of solvents by distillation in all-glass systems may be required.

6.6 Sodium sulfate—(ACS) granular, anhydrous, rinsed or Soxhlet extracted with methylene chloride (20 mL/g), baked at in a shallow tray at 450 °C for one hour minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw cap that prevents moisture from entering.

6.7 Stock standard solutions (1.00 µg/µL)—Stock standard solutions may be prepared from pure materials, or purchased as certified solutions. Traceability must be to the National Institute of Standards and Technology (NIST) or other national standard, when available. Stock solution concentrations alternate to those below may be used. Because of the toxicity of some of the compounds, primary dilutions should be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations of neat materials are handled. The following procedure may be used to prepare standards from neat materials.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality methanol or other suitable solvent and dilute to volume in a 10 mL volumetric flask. Larger volumes may be used at the convenience of the laboratory. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards

may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 Transfer the stock standard solutions to fluoropolymer-sealed screw-cap bottles. Store at <6 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.3 Replace purchased certified stock standard solutions per the expiration date. Replace stock standard solutions prepared by the laboratory or mixed with purchased solutions after one year, or sooner if comparison with QC check samples indicates a problem.

6.8 Surrogate standard spiking solution

6.8.1 Select a minimum of three surrogate compounds from Table 8 that most closely match the recovery of the analytes of interest. For example, if all analytes tested are considered acids, use surrogates that have similar chemical attributes. Other compounds may be used as surrogates so long as they do not interfere in the analysis. The deuterium and carbon-13 labeled compounds in Method 1625B are particularly useful because Method 1625B contains QC acceptance criteria for recovery of these compounds. If only one or two analytes are determined, one or two surrogates may be used.

6.8.2 Prepare a solution containing each selected surrogate such that the concentration in the sample would match the concentration in the mid-point calibration standard. For example, if the midpoint of the calibration is 100 µg/L, prepare the spiking solution at a concentration of 100 µg/mL in methanol. Addition of 1.00 mL of this solution to 1000 mL of sample will produce a concentration of 100 µg/L of the surrogate. Alternate volumes and concentrations appropriate to the response of the GC/MS instrument or for selective ion monitoring (SIM) may be used, if desired.

6.8.3 Store the spiking solution at ≤ 6°C in a fluoropolymer-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after one year, or sooner if comparison with quality control check standards indicates a problem.

6.9 Internal standard spiking solution

6.9.1 Select three or more internal standards similar in chromatographic behavior to the analytes of interest. Internal standards are listed in Table 8. Suggested internal standards are: 1,4-dichlorobenzene-d_4; naphthalene-d_8; acenaphthene-d_{10}; phenanthrene-d_{10}; chrysene-d_{12}; and perylene-d_{12}. The laboratory must demonstrate that measurement of the internal standards is not affected by method or matrix interferences (see also Section 7.3.4).

6.9.2 Prepare the internal standards at a concentration of 10 mg/mL in methylene chloride or other suitable solvent. When 10 µL of this solution is spiked into a 1-mL extract, the concentration of the internal standards will be 100 µg/mL. A lower concentration appropriate to the response of the GC/MS instrument or for SIM may be used, if desired.

6.9.3 To assure accurate analyte identification, particularly when SIM is used, it may be advantageous to include more internal standards than those suggested in Section 6.9.1. An analyte will be located most accurately if its retention time relative to an internal standard is in the range of 0.8 to 1.2.

6.10 DFTPP standard—Prepare a solution of DFTPP in methanol or other suitable solvent such that 50 ng or less will be injected (see Section 13.2). An alternate concentration may be used to compensate for specific injection volumes or to assure that the operating range of the instrument is not exceeded, so long as the total injected is 50 ng or less. Include benzidine and pentachlorophenol in this solution such that ≤100 ng of benzidine and ≤50 ng of pentachlorophenol will be injected.

6.11 Quality control check sample concentrate—See Section 8.2.1.

6.12 GPC calibration solution

6.12.1 Prepare a methylene chloride solution to contain corn oil, bis(2-ethylhexyl) phthalate (BEHP), perylene, and sulfur at the concentrations in Section 6.12.2, or at concentrations appropriate to the response of the detector.

Note: Sulfur does not readily dissolve in methylene chloride, but is soluble in warm corn oil. The following procedure is suggested for preparation of the solution:

6.12.2 Weigh 8 mg sulfur and 2.5 g corn oil into a 100-mL volumetric flask and warm to dissolve the sulfur. Separately weigh 100 mg BEHP and 2 mg perylene and add to flask. Bring to volume with methylene chloride and mix thoroughly.

6.12.3 Store the solution in an amber glass bottle with a fluoropolymer-lined screw cap at 0–6 °C. Protect from light. Refrigeration may cause the corn oil to precipitate. Before use, allow the solution to stand at room temperature until the corn oil dissolves, or warm slightly to aid in dissolution. Replace the solution every year, or more frequently if the response of a component changes.

6.13 Sulfur removal—Copper foil or powder (bright, non-oxidized), or tetrabutylammonium sulfite (TBA sulfite).

6.13.1 Copper foil, or powder—Fisher, Alfa Aesar 42455–18, 625 mesh, or equivalent. Cut copper foil into approximately 1-cm squares. Copper must be activated on each day it will be used, as follows:

6.13.1.1 Place the quantity of copper needed for sulfur removal (Section 11.2.1.3) in a ground-glass-stoppered Erlenmeyer flask or bottle. Cover the foil or powder with methanol.

6.13.1.2 Add HCl dropwise (0.5–1.0 mL) while swirling, until the copper brightens.

6.13.1.3 Pour off the methanol/HCl and rinse 3 times with reagent water to remove all traces of acid, then 3 times with acetone, then 3 times with hexane.

6.13.1.4 For copper foil, cover with hexane after the final rinse. Store in a stoppered flask under nitrogen until used. For the powder, dry on a rotary evaporator or under a stream of nitrogen. Store in a stoppered flask under nitrogen until used.

6.13.2 Tetrabutylammonium sodium sulfite (TBA sodium sulfite).

6.13.2.1 Tetrabutylammonium hydrogen sulfate, $[CH_3(CH_2)_3]_4NHSO_4$.

6.13.2.2 Sodium sulfite, Na_2SO_3.

6.13.2.3 Dissolve approximately 3 g tetrabutylammonium hydrogen sulfate in 100 mL of reagent water in an amber bottle with fluoropolymer-lined screw cap. Extract with three 20-mL portions of hexane and discard the hexane extracts.

6.13.2.4 Add 25 g sodium sulfite to produce a saturated solution. Store at room temperature. Replace after 1 month.

7. Calibration

7.1 Establish operating conditions equivalent to those in the footnote to Table 4 or 5 for the base/neutral or acid fraction, respectively. If a combined base/neutral/acid fraction will be analyzed, use the conditions in the footnote to Table 4. Alternative temperature program and flow rate conditions may be used. It is necessary to calibrate the GC/MS for the analytes of interest (Section 1.3) only.

7.2 Internal standard calibration

7.2.1 Prepare calibration standards for the analytes of interest and surrogates at a minimum of five concentration levels by adding appropriate volumes of one or more stock standards to volumetric flasks. One of the calibration standards should be at a concentration near the ML for the analyte in Table 1, 2, or 3. The ML value may be rounded to a whole number that

is more convenient for preparing the standard, but must not exceed the ML values listed in Table 1, 2, or 3 for those analytes which list ML values. Alternatively, the laboratory may establish the ML for each analyte based on the concentration of the lowest calibration standard in a series of standards obtained from a commercial vendor, again, provided that the ML values do not exceed the MLs in Tables 1, 2, or 3, and provided that the resulting calibration meets the acceptance criteria in Section 7.2.3, based on the RSD, RSE, or R^2.

The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system for full-scan and/or SIM operation, as appropriate. A minimum of six concentration levels is required for a second order, non-linear (*e.g.,* quadratic; $ax^2 + bx + c$) calibration. Calibrations higher than second order are not allowed. To each calibration standard or standard mixture, add a known constant volume of the internal standard solution (Section 6.9), and dilute to volume with methylene chloride.

Note: The large number of analytes in Tables 1 through 3 may not be soluble or stable in a single solution; multiple solutions may be required if a large number of analytes are to be determined simultaneously.

7.2.1.1 Prior to analysis of the calibration standards, inject the DFTPP standard (Section 6.10) and adjust the scan rate of the mass spectrometer to produce a minimum of 5 mass spectra across the DFTPP GC peak. Adjust instrument conditions until the DFTPP criteria in Table 9A or 9B are met. Calculate peak tailing factors for benzidine and pentachlorophenol. Calculation of the tailing factor is illustrated in Figure 1. The tailing factor for benzidine and pentachlorophenol must be <2; otherwise, adjust instrument conditions and either replace the column or break off a short section of the front end of the column, and repeat the test.

Note: The DFTPP spectrum may be evaluated by summing the intensities of the m/z's across the GC peak, subtracting the background at each m/z in a region of the chromatogram within 20 scans of but not including any part of, the DFTPP peak. The DFTPP spectrum may also be evaluated by fitting a Gaussian to each m/z and using the intensity at the maximum for each Gaussian or by integrating the area at each m/z and using the integrated areas. Other means may be used for evaluation of the DFTPP spectrum so long as the spectrum is not distorted to meet the criteria in Table 9A or 9B.

7.2.1.2 Analyze the mid-point combined base/neutral and acid calibration standard and enter or review the retention time, relative retention time, mass spectrum, and quantitation m/z in the data system for each analyte of interest, surrogate, and internal standard. If additional analytes (Table 3) are to be quantified, include these analytes in the standard. The mass spectrum for each analyte must be comprised of a minimum of 2 m/z's (Tables 4 and 5); 3 to 5 m/z's assure more reliable analyte identification. Suggested quantitation m/z's are shown in Tables 4 and 5 as the primary m/z. If an interference occurs at the primary m/z, use one of the secondary m/z's or an alternate m/z. A single m/z only is required for quantitation.

7.2.1.3 For SIM operation, determine the analytes in each descriptor, the quantitation and qualifier m/z's for each analyte (the m/z's can be the same as for full-scan operation; Section 7.2.1.2), the dwell time on each m/z for each analyte, and the beginning and ending retention time for each descriptor. Analyze the verification standard in scan mode to verify m/z's and establish the retention times for the analytes. There must be a minimum of two m/z's for each analyte to assure analyte identification. To maintain sensitivity and capture enough scans (≥5) across each chromatographic peak, there should be no more than 10 m/z's in a descriptor. For example, for a descriptor with 10 m/z's and a chromatographic peak width of 5 sec, a dwell time of 100 ms at each m/z would result in a scan time of 1 second and provide 5 scans across the GC peak. The quantitation m/z will usually be the most intense peak in the mass spectrum. The quantitation m/z and dwell time may be optimized for each analyte. However, if a GC peak spans two (or more) descriptors, the dwell time and cycle time (scans/sec) should be set to the same value in both segments in order to maintain equivalent response. The acquisition table used for SIM must take into account the mass defect (usually less than 0.2 Daltons) that can occur at each m/z being monitored.

7.2.1.4 For combined scan and SIM operation, set up the scan segments and descriptors to meet requirements in Sections 7.2.1.1–7.2.1.3.

7.2.2 Analyze each calibration standard according to Section 12 and tabulate the area at the quantitation m/z against concentration for each analyte of interest, surrogate, and internal standard. If an interference is encountered, use a secondary m/z (Table 4 or 5) for quantitation. Calculate a response factor (RF) for each analyte of interest at each concentration using Equation 1.

$$RF = \frac{(A_s x C_{is})}{(A_{is} x C_s)}$$

Equation 1

Where:

A_s = Area of the characteristic m/z for the analyte of interest or surrogate.

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard (µg/mL).

C_s = Concentration of the analyte of interest or surrogate (µg/mL).

7.2.3 Calculate the mean (average) and relative standard deviation (RSD) of the responses factors. If the RSD is less than 35%, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to fit a linear or quadratic regression of response ratios, As/Ais, vs. concentration ratios Cs/Cis. If used, the regression must be weighted inversely proportional to concentration. The coefficient of determination (R^2; Reference 10) of the weighted regression must be greater than 0.920. Alternatively, the relative standard error (Reference 11) may be used as an acceptance criterion. As with the RSD, the RSE must be less than 35%. If an RSE less than 35% cannot be achieved for a quadratic regression, system performance is unacceptable and the system must be adjusted and re-calibrated.

Note: Using capillary columns and current instrumentation, it is quite likely that a laboratory can calibrate the target analytes in this method and achieve a linearity metric (either RSD or RSE) well below 35%. Therefore, laboratories are permitted to use more stringent acceptance criteria for calibration than described here, for example, to harmonize their application of this method with those from other sources.

7.3 Calibration verification—The RF or calibration curve must be verified immediately after calibration and at the beginning of each 12-hour shift, by analysis of a mid-point calibration standard (Section 7.2.1). The standard(s)

must be obtained from a second manufacturer or a manufacturer's batch prepared independently from the batch used for calibration. Traceability must be to a national standard, when available. The concentration of the standard should be near the mid-point of the calibration. Include the surrogates (Section 6.8) in this solution. It is necessary to verify calibration for the analytes of interest (Section 1.3) only.

Note: The 12-hour shift begins after the DFTPP (Section 13.1) and DDT/endrin tests (if DDT and endrin are to be determined), and after analysis of the calibration verification standard. The 12-hour shift ends 12 hours later. The DFTPP and DDT/endrin tests are outside of the 12-hour shift.

7.3.1 Analyze the calibration verification standard(s) beginning in Section 12. Calculate the percent recovery of each analyte. Compare the recoveries for the analytes of interest against the acceptance criteria for recovery (Q) in Table 6, and the recoveries for the surrogates against the acceptance criteria in Table 8. If recovery of the analytes of interest and surrogates meet acceptance criteria, system performance is acceptable and analysis of samples may continue. If any individual recovery is outside its limit, system performance is unacceptable for that analyte.

Note: The large number of analytes in Tables 6 and 8 present a substantial probability that one or more will fail acceptance criteria when all analytes are tested simultaneously.

7.3.2 When one or more analytes fail acceptance criteria, analyze a second aliquot of the calibration verification standard and compare only those analytes that failed the first test (Section 7.3.1) with their respective acceptance criteria. If these analytes now pass, system performance is acceptable and analysis of samples may continue. A repeat failure of any analyte that failed the first test, however, will confirm a general problem with the measurement system. If this occurs, repair the system (Section 7.2.1.1) and repeat the test (Section 7.3.1), or prepare a fresh calibration standard and repeat the test. If calibration cannot be verified after maintenance or injection of the fresh calibration standard, re-calibrate the instrument.

Note: If it is necessary to perform a repeat verification test frequently; *i.e.,* perform two tests in order to pass, it may be prudent to perform two injections in succession and review the results, rather than perform one injection, review the results, then perform the second injection if results from the first injection fail. To maintain the validity of the test and re-test, system maintenance and/or adjustment is not permitted between the injections.

7.3.3 Many of the analytes in Table 3 do not have QC acceptance criteria in Table 6, and some of the surrogates in Table 8 do not have acceptance criteria. If calibration is to be verified and other QC tests are to be performed for these analytes, acceptance criteria must be developed and applied. EPA has provided guidance for development of QC acceptance criteria (References 12 and 13).

7.3.4 Internal standard responses—Verify that detector sensitivity has not changed by comparing the response of each internal standard in the calibration verification standard (Section 7.3) to the response of the respective internal standard in the midpoint calibration standard (Section 7.2.1). The peak areas or heights of the internal standards in the calibration verification standard must be within 50% to 200% (½ to 2x) of their respective peak areas or heights in the mid-point calibration standard. If not, repeat the calibration verification test using a fresh calibration verification standard (7.3), or perform and document system repair. Subsequent to repair, repeat the calibration verification test (Section 7.3.1). If the responses are still not within 50% to 200%, re-calibrate the instrument (Section 7.2.2) and repeat the calibration verification test.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and ongoing analysis of spiked samples and blanks to evaluate and document data quality (40 CFR 136.7). The laboratory must maintain records to document the quality of data generated. Results of ongoing performance tests are compared with established QC acceptance criteria to determine if the results of analyses meet performance requirements of this method. When results of spiked samples do not meet the QC acceptance criteria in this method, a quality control check sample (laboratory control sample; LCS) must be analyzed to confirm that the measurements were performed in an in-control mode of operation. A laboratory may develop its own performance criteria (as QC acceptance criteria), provided such criteria are as or more restrictive than the criteria in this method.

8.1.1 The laboratory must make an initial demonstration of capability (DOC) to generate acceptable precision and recovery with this method. This demonstration is detailed in Section 8.2.

8.1.2 In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory is permitted certain options (Section 1.6 and 40 CFR 136.6(b)) to improve separations or lower the costs of measurements. These options may include alternate extraction, concentration, and cleanup procedures (*e.g.,* solid-phase extraction; rotary-evaporator concentration; column chromatography cleanup), changes in column and type of mass spectrometer (40 CFR 136.6(b)(4)(xvi)). Alternate determinative techniques, such as substitution of spectroscopic or immunoassay techniques, and changes that degrade method performance, are not allowed. If an analytical technique other than GC/MS is used, that technique must have a specificity equal to or greater than the specificity of GC/MS for the analytes of interest. The laboratory is also encouraged to participate in inter-comparison and performance evaluation studies (see Section 8.10).

8.1.2.1 Each time a modification is made to this method, the laboratory is required to repeat the procedure in Section 8.2. If the detection limit of the method will be affected by the change, the laboratory must demonstrate that the MDLs (40 CFR part 136, appendix B) are lower than one-third the regulatory compliance limit or the MDLs in this method, whichever are greater. If calibration will be affected by the change, the instrument must be recalibrated per Section 7. Once the modification is demonstrated to produce results equivalent or superior to results produced by this method, that modification may be used routinely thereafter, so long as the other requirements in this method are met (*e.g.,* matrix spike/matrix spike duplicate recovery and relative percent difference).

8.1.2.1.1 If SPE, or another allowed method modification, is to be applied to a specific discharge, the laboratory must prepare and analyze matrix spike/matrix spike duplicate (MS/MSD) samples (Section 8.3) and LCS samples (Section 8.4). The laboratory must include surrogates (Section 8.7) in each of the samples. The MS/MSD and LCS samples must be fortified with the analytes of interest (Section 1.3). If the modification is for nationwide use, MS/MSD samples must be prepared from a minimum of nine different discharges (See Section 8.1.2.1.2), and all QC acceptance criteria in this method must be met. This evaluation only needs to be performed once other than for the routine QC required by this method (for example it could be performed by the

vendor of the SPE materials) but any laboratory using that specific SPE material must have the results of the study available. This includes a full data package with the raw data that will allow an independent reviewer to verify each determination and calculation performed by the laboratory (see Section 8.1.2.2.5, items a–q).

8.1.2.1.2 Sample matrices on which MS/MSD tests must be performed for nationwide use of an allowed modification:

(a) Effluent from a POTW.

(b) ASTM D5905 Standard Specification for Substitute Wastewater.

(c) Sewage sludge, if sewage sludge will be in the permit.

(d) ASTM D1141 Standard Specification for Substitute Ocean Water, if ocean water will be in the permit.

(e) Untreated and treated wastewaters up to a total of nine matrix types (see *http://water.epa.gov/scitech/wastetech/guide/industry.cfm*) for a list of industrial categories with existing effluent guidelines).

At least one of the above wastewater matrix types must have at least one of the following characteristics:

(i) Total suspended solids greater than 40 mg/L.

(ii) Total dissolved solids greater than 100 mg/L.

(iii) Oil and grease greater than 20 mg/L.

(iv) NaCl greater than 120 mg/L.

(v) $CaCO_3$ greater than 140 mg/L.

The interim acceptance criteria for MS, MSD recoveries that do not have recovery limits specified in Table 6, and recoveries for surrogates that do not have recovery limits specified in Table 8, must be no wider than 60–140%, and the relative percent difference (RPD) of the concentrations in the MS and MSD that do not have RPD limits specified in Table 6 must be less than 30%. Alternatively, the laboratory may use the laboratory's in-house limits if they are tighter.

(f) A proficiency testing (PT) sample from a recognized provider, in addition to tests of the nine matrices (Section 8.1.2.1.1).

8.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

8.1.2.2.1 The names, titles, street addresses, telephone numbers, and email addresses of the analyst(s) that performed the analyses and modification, and of the quality control officer that witnessed and will verify the analyses and modifications.

8.1.2.2.2 A list of analytes, by name and CAS Registry Number.

8.1.2.2.3 A narrative stating reason(s) for the modifications.

8.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

(a) Calibration (Section 7).

(b) Calibration verification (Section 7).

(c) Initial demonstration of capability (Section 8.2).

(d) Analysis of blanks (Section 8.5).

(e) Matrix spike/matrix spike duplicate analysis (Section 8.3).

(f) Laboratory control sample analysis (Section 8.4).

8.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

(a) Sample numbers and other identifiers.

(b) Extraction dates.

(c) Analysis dates and times.

(d) Analysis sequence/run chronology.

(e) Sample weight or volume (Section 10).

(f) Extract volume prior to each cleanup step (Sections 10 and 11).

(g) Extract volume after each cleanup step (Section 11).

(h) Final extract volume prior to injection (Sections 10 and 12).

(i) Injection volume (Section 12.2.3).

(j) Sample or extract dilution (Section 12.2.3.2).

(k) Instrument and operating conditions.

(l) Column (dimensions, material, etc).

(m) Operating conditions (temperature program, flow rate, etc).

(n) Detector (type, operating conditions, etc).

(o) Chromatograms, mass spectra, and other recordings of raw data.

(p) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.

(q) A written Standard Operating Procedure (SOP).

8.1.2.2.6 Each individual laboratory wishing to use a given modification must perform the start-up tests in Section 8.1.2 (*e.g.,* DOC, MDL), with the modification as an integral part of this method prior to applying the modification to specific discharges. Results of the DOC must meet the QC acceptance criteria in Table 6 for the analytes of interest (Section 1.3), and the MDLs must be equal to or lower than the MDLs in Tables 4 and 5 for the analytes of interest.

8.1.3 Before analyzing samples, the laboratory must analyze a blank to demonstrate that interferences from the analytical system, labware, and reagents, are under control. Each time a batch of samples is extracted or reagents are changed, a blank must be extracted and analyzed as a safeguard against laboratory contamination. Requirements for the blank are given in Section 8.5.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of one sample, in duplicate, with the samples in an extraction batch (Section 3.1). The laboratory must also spike and analyze, in duplicate, a minimum of 5% of all samples from a given site or discharge to monitor and evaluate method and laboratory performance on the sample matrix. The batch and site/discharge samples may be the same. The procedure for spiking and analysis is given in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through analysis of a quality control check sample (laboratory control sample, LCS; on-going precision and recovery sample, OPR) that the measurement system is in control. This procedure is given in Section 8.4.

8.1.6 The laboratory should maintain performance records to document the quality of data that is generated. This procedure is given in Section 8.9.

8.1.7 The large number of analytes tested in performance tests in this method present a substantial probability that one or more will fail acceptance criteria when many analytes are tested simultaneously, and a re-test is allowed if this situation should occur. If, however, continued re-testing results in further repeated failures, the laboratory should document the failures (*e.g.,* as qualifiers on results) and either avoid reporting results for analytes that failed or report the problem and failures with the data. Failure to report does not relieve a discharger or permittee of reporting timely results.

8.2 Initial demonstration of capability (DOC)—To establish the ability to generate acceptable recovery and precision, the laboratory must perform the DOC in Sections 8.2.1 through 8.2.6 for the analytes of interest. The laboratory must also establish MDLs for the analytes of interest using the MDL procedure at 40 CFR part 136, appendix B. The laboratory's MDLs must be equal to or lower than those listed in Tables 1, 2, or 3 or lower than one third the regulatory compliance limit, whichever is greater. For MDLs not listed in Tables 4 and 5, the laboratory must determine the MDLs using the MDL procedure at 40 CFR 136, Appendix B under the same conditions used to determine the MDLs for the analytes listed in Tables 1, 2, and 3. All

procedures used in the analysis, including cleanup procedures, must be included in the DOC.

8.2.1 For the DOC, a QC check sample concentrate containing each analyte of interest (Section 1.3) is prepared in a water-miscible solvent. The QC check sample concentrate must be prepared independently from those used for calibration, but may be from the same source as the second-source standard used for calibration verification (Section 7.3). The concentrate should produce concentrations of the analytes of interest in water at the mid-point of the calibration range, and may be at the same concentration as the LCS (Section 8.4). Multiple solutions may be required.

Note: QC check sample concentrates are no longer available from EPA.

8.2.2 Using a pipet or micro-syringe, prepare four LCSs by adding an appropriate volume of the concentrate to each of four 1–L aliquots of reagent water, and mix well. The volume of reagent water must be the same as the volume that will be used for the sample, blank (Section 8.5), and MS/MSD (Section 8.3). A concentration of 100 µg/L was used to develop the QC acceptance criteria in Table 6. Also add an aliquot of the surrogate spiking solution (Section 6.8). Also add an aliquot of the surrogate spiking solution (Section 6.8) to the reagent-water aliquots.

8.2.3 Extract and analyze the four LCSs according to the method beginning in Section 10.

8.2.4 Calculate the average percent recovery ($\bar{x}$) and the standard deviation of the percent recovery(s) for each analyte using the four results.

8.2.5 For each analyte, compare s and ($\bar{x}$) with the corresponding acceptance criteria for precision and recovery in Table 6. For analytes in Table 3 not listed in Table 6, DOC QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 12 and 13). If s and ($\bar{x}$) for all analytes of interest meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If any individual s exceeds the precision limit or any individual ($\bar{x}$) falls outside the range for recovery, system performance is unacceptable for that analyte.

Note: The large number of analytes in Tables 1–3 present a substantial probability that one or more will fail at least one of the acceptance criteria when many or all analytes are determined simultaneously. Therefore, the analyst is permitted to conduct a ''re-test'' as described in Sec. 8.2.6.

8.2.6 When one or more of the analytes tested fail at least one of the acceptance criteria, repeat the test for only the analytes that failed. If results for these analytes pass, system performance is acceptable and analysis of samples and blanks may proceed. If one or more of the analytes again fail, system performance is unacceptable for the analytes that failed the acceptance criteria. Correct the problem and repeat the test (Section 8.2). See Section 8.1.7 for disposition of repeated failures.

Note: To maintain the validity of the test and re-test, system maintenance and/or adjustment is not permitted between this pair of tests.

8.3 Matrix spike and matrix spike duplicate (MS/MSD)—The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored in duplicate to assess accuracy (recovery and precision). The data user should identify the sample and the analytes of interest (Section 1.3) to be spiked. If direction cannot be obtained, the laboratory must spike at least one sample per extraction batch of up to 20 samples with the analytes in Tables 1 and 2. Spiked sample results should be reported only to the data user whose sample was spiked, or as requested or required by a regulatory/control authority.

8.3.1 If, as in compliance monitoring, the concentration of a specific analyte will be checked against a regulatory concentration limit, the concentration of the spike should be at that limit; otherwise, the concentration of the spike should be one to five times higher than the background concentration determined in Section 8.3.2, at or near the midpoint of the calibration range, or at the concentration in the LCS (Section 8.4) whichever concentration would be larger.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of the each analyte of interest. If necessary, prepare a new check sample concentrate (Section 8.2.1) appropriate for the background concentration. Spike and analyze two additional sample aliquots, and determine the concentration after spiking (A_1 and A_2) of each analyte. Calculate the percent recoveries (P_1 and P_2) as $100\ (A_1 - B)/T$ and $100\ (A_2 - B)/T$, where T is the known true value of the spike. Also calculate the relative percent difference (RPD) between the concentrations (A_1 and A_2) as $200|A_1 - A_2|/(A_1 + A_2)$. If necessary, adjust the concentrations used to calculate the RPD to account for differences in the volumes of the spiked aliquots.

8.3.3 Compare the percent recoveries (P_1 and P_2) and the RPD for each analyte in the MS/MSD aliquots with the corresponding QC acceptance criteria in Table 6. A laboratory may develop and apply QC acceptance criteria more restrictive than the criteria in Table 6, if desired.

8.3.3.1 If any individual P falls outside the designated range for recovery in either aliquot, or the RPD limit is exceeded, the result for the analyte in the unspiked sample is suspect and may not be reported or used for permitting or regulatory compliance purposes. See Section 8.1.7 for disposition of failures.

8.3.3.2 The acceptance criteria in Table 6 were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the spike to background ratio approaches 5:1 (Reference 14). If spiking is performed at a concentration lower than 100 µg/L, the laboratory must use either the QC acceptance criteria in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To use the optional acceptance criteria: (1) Calculate recovery (X′) using the equation in Table 7, substituting the spike concentration (T) for C; (2) Calculate overall precision (S′) using the equation in Table 7, substituting X′ for $\bar{x}$; (3) Calculate the range for recovery at the spike concentration as $(100\ X'/T) \pm 2.44(100\ S'/T)\%$ (Reference 14). For analytes in Table 3 not listed in Table 6, QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 12 and 13).

8.3.4 After analysis of a minimum of 20 MS/MSD samples for each target analyte and surrogate, the laboratory must calculate and apply in-house QC limits for recovery and RPD of future MS/MSD samples (Section 8.3). The QC limits for recovery are calculated as the mean observed recovery ± 3 standard deviations, and the upper QC limit for RPD is calculated as the mean RPD plus 3 standard deviations of the RPDs. The in-house QC limits must be updated at least every two years and re-established after any major change in the analytical instrumentation or process. At least 80% of the analytes tested in the MS/MSD must have in-house QC acceptance criteria that are tighter than those in Table 6. If an in-house QC limit for the RPD is greater than the limit in Table 6,

then the limit in Table 6 must be used. Similarly, if an in-house lower limit for recovery is below the lower limit in Table 6, then the lower limit in Table 6 must be used, and if an in-house upper limit for recovery is above the upper limit in Table 6, then the upper limit in Table 6 must be used. The laboratory must evaluate surrogate recovery data in each sample against its in-house surrogate recovery limits. The laboratory may use 60–140% as interim acceptance criteria for surrogate recoveries until in-house limits are developed.

8.4 Laboratory control sample (LCS)—A QC check sample (laboratory control sample, LCS; on-going precision and recovery sample, OPR) containing each analyte of interest (Section 1.3) and surrogate must be prepared and analyzed with each extraction batch of up to 20 samples to demonstrate acceptable recovery of the analytes of interest from a clean sample matrix.

8.4.1 Prepare the LCS by adding QC check sample concentrate (Section 8.2.1) to reagent water. Include all analytes of interest (Section 1.3) in the LCS. The LCS may be the same sample prepared for the DOC (Section 8.2.1). The volume of reagent water must be the same as the volume used for the sample, blank (Section 8.5), and MS/MSD (Section 8.3). Also add an aliquot of the surrogate spiking solution (Section 6.8). The concentration of the analytes in reagent water should be the same as the concentration in the DOC (Section 8.2.2).

8.4.2 Analyze the LCS prior to analysis of field samples in the extraction batch. Determine the concentration (A) of each analyte. Calculate the percent recovery (PS) as 100 (A/T)%, where T is the true value of the concentration in the LCS.

8.4.3 Compare the percent recovery (PS) for each analyte with its corresponding QC acceptance criterion in Table 6. For analytes of interest in Table 3 not listed in Table 6, use the QC acceptance criteria developed for the MS/MSD (Section 8.3.3.2). If the recoveries for all analytes of interest fall within their respective QC acceptance criteria, analysis of blanks and field samples may proceed. If any individual PS falls outside the range, proceed according to Section 8.4.4.

Note: The large number of analytes in Tables 1–3 present a substantial probability that one or more will fail the acceptance criteria when all analytes are tested simultaneously. Because a re-test is allowed in event of failure (Sections 8.1.7 and 8.4.3), it may be prudent to extract and analyze two LCSs together and evaluate results of the second analysis against the QC acceptance criteria only if an analyte fails the first test.

8.4.4 Repeat the test only for those analytes that failed to meet the acceptance criteria (PS). If these analytes now pass, system performance is acceptable and analysis of blanks and samples may proceed. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, repeat the test using a fresh LCS (Section 8.2.2) or an LCS prepared with a fresh QC check sample concentrate (Section 8.2.1), or perform and document system repair. Subsequent to repair, repeat the LCS test (Section 8.4). If failure of the LCS indicates a systemic problem with samples in the batch, re-extract and re-analyze the samples in the batch. See Section 8.1.7 for disposition of repeated failures.

Note: To maintain the validity of the test and re-test, system maintenance and/or adjustment is not permitted between the pair of tests.

8.4.5 After analysis of 20 LCS samples, the laboratory must calculate and apply in-house QC limits for recovery to future LCS samples (Section 8.4). Limits for recovery in the LCS are calculated as the mean recovery ±3 standard deviations. A minimum of 80% of the analytes tested for in the LCS must have QC acceptance criteria tighter than those in Table 6. Many of the analytes and surrogates may not contain recommended acceptance criteria. The laboratory should use 60–140% as interim acceptance criteria for recoveries of spiked analytes and surrogates that do not have recovery limits specified in Table 8, until in-house LCS and surrogate limits are developed. If an in-house lower limit for recovery is lower than the lower limit in Table 6, the lower limit in Table 6 must be used, and if an in-house upper limit for recovery is higher than the upper limit in Table 6, the upper limit in Table 6 must be used.

8.5 Blank—A blank must be extracted and analyzed with each extraction batch to demonstrate that the reagents and equipment used for preparation and analysis are free from contamination.

8.5.1 Spike the surrogates into the blank. Extract and concentrate the blank using the same procedures and reagents used for the samples, LCS, and MS/MSD in the batch. Analyze the blank immediately after analysis of the LCS (Section 8.4) and prior to analysis of the MS/MSD and samples to demonstrate freedom from contamination.

8.5.2 If any analyte of interest is found in the blank: 1) At a concentration greater than the MDL for the analyte, 2) at a concentration greater than one-third the regulatory compliance limit, or 3) at a concentration greater than one-tenth the concentration in a sample in the extraction batch, whichever is greater, analysis of samples must be halted and samples affected by the blank must be re-extracted and the extracts re-analyzed. Samples must be associated with an uncontaminated blank before they may be reported or used for permitting or regulatory compliance purposes.

8.6 Internal standards responses.

8.6.1 Calibration verification—The responses (GC peak heights or areas) of the internal standards in the calibration verification must be within 50% to 200% (½ to 2x) of their respective responses in the mid-point calibration standard. If they are not, repeat the calibration verification (Section 7.4) test or perform and document system repair. Subsequent to repair, repeat the calibration verification. If the responses are still not within 50% to 200%, re-calibrate the instrument (Section 7) and repeat the calibration verification/LCS test.

8.6.2 Samples, blanks, LCSs, and MS/MSDs—The responses (GC peak heights or areas) of the internal standards in each sample, blank, and MS/MSD must be within 50% to 200% (½ to 2x) of its respective response in the most recent LCS. If, as a group, all internal standards are not within this range, perform and document system repair, repeat the calibration verification/LCS test (Section 8.4), and re-analyze the affected samples. If a single internal standard is not within the 50% to 200% range, use an alternate internal standard for quantitation of the analyte referenced to the affected internal standard.

8.7 Surrogate recoveries—Spike the surrogates into all samples, blanks, LCSs, and MS/MSDs. Compare surrogate recoveries against the QC acceptance criteria in Table 8 and/or those developed in Section 7.3.3. If any recovery fails its criteria, attempt to find and correct the cause of the failure. Surrogate recoveries from the blank and LCS may be used as pass/fail criteria by the laboratory or as required by a regulatory authority, or may be used to diagnose problems with the analytical system.

8.8 DDT and endrin decomposition (breakdown)—If DDT and/or endrin are to be analyzed using this method, a DDT/endrin decomposition test must be performed to reliably quantify these two pesticides. The DDT/endrin decomposition test to be used is in EPA Method 608A or 1656.

8.9 As part of the QC program for the laboratory, control charts or statements of accuracy for wastewater samples must be assessed and records maintained (40 CFR 136.7(c)(1)(viii)). After analysis of five or more spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{x}$) and the standard deviation of the percent recovery (sp). Express the accuracy assessment as a percent interval from $\bar{x} - 2sp$ to $\bar{x} + 2sp$. For example, if $\bar{x}$ = 90% and sp = 10%, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each analyte on a regular basis (*e.g.,* after each 5–10 new accuracy measurements).

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Collect samples as grab samples in glass bottles or in refrigerated bottles using automatic sampling equipment. Collect 1–L of ambient waters, effluents, and other aqueous samples. If the sensitivity of the analytical system is sufficient, a smaller volume (*e.g.,* 250 mL), but no less than 100 mL, may be used. Conventional sampling practices (Reference 15) should be followed, except that the bottle must not be pre-rinsed with sample before collection. Automatic sampling equipment must be as free as possible of polyvinyl chloride or other tubing or other potential sources of contamination. If needed, collect additional sample(s) for the MS/MSD (Section 8.3).

9.2 Ice or refrigerate samples at ≤6 °C from the time of collection until extraction, but do not freeze. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. Any method suitable for field use may be employed to test for residual chlorine (Reference 16). Do not add excess sodium thiosulfate. If sodium thiosulfate interferes in the determination of the analytes, an alternate preservative (*e.g.,* ascorbic acid or sodium sulfite) may be used.

9.3 All samples must be extracted within 7 days of collection and sample extracts must be analyzed within 40 days of extraction.

10. Extraction

10.1 This section contains procedures for separatory funnel liquid-liquid extraction (SFLLE) and continuous liquid-liquid extraction (CLLE). SFLLE is faster, but may not be as effective as CLLE for recovery of polar analytes such as phenol. SFLLE is labor intensive and may result in formation of emulsions that are difficult to break. CLLE is less labor intensive, avoids emulsion formation, but requires more time (18–24 hours) and more hood space, and may require more solvent. The procedures assume base-neutral extraction followed by acid extraction. For some matrices and analytes of interest, improved results may be obtained by acid-neutral extraction followed by base extraction. A single acid or base extraction may also be performed. If an extraction scheme alternate to base-neutral followed by acid extraction is used, all QC tests must be performed and all QC acceptance criteria must be met with that extraction scheme as an integral part of this method.

10.2 Separatory funnel liquid-liquid extraction (SFLLE) and extract concentration

10.2.1 The SFLLE procedure below assumes a sample volume of 1 L. When a different sample volume is extracted, adjust the volume of methylene chloride accordingly.

10.2.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into the separatory funnel. Pipet the surrogate standard spiking solution (Section 6.8) into the separatory funnel. If the sample will be used for the LCS or MS or MSD, pipet the appropriate check sample concentrate (Section 8.2.1 or 8.3.2) into the separatory funnel. Mix well. Check the pH of the sample with wide-range pH paper and adjust to pH 11–13 with sodium hydroxide solution.

10.2.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake for approximately 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a flask. If the emulsion cannot be broken (recovery of <80% of the methylene chloride), transfer the sample, solvent, and emulsion into a continuous extractor and proceed as described in Section 10.3.

10.2.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.2.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Serially extract the acidified aqueous phase three times with 60 mL aliquots of methylene chloride. Collect and combine the extracts in a flask in the same manner as the base/neutral extracts.

Note: Base/neutral and acid extracts may be combined for concentration and analysis provided all QC tests are performed and all QC acceptance criteria met for the analytes of interest with the combined extract as an integral part of this method, and provided that the analytes of interest are as reliably identified and quantified as when the extracts are analyzed separately. If doubt exists as to whether identification and quantitation will be affected by use of a combined extract, the fractions must be analyzed separately.

10.2.6 For each fraction or the combined fractions, assemble a Kuderna-Danish (K–D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K–D concentrator so long as the requirements in Section 8.2 are met.

10.2.7 For each fraction or the combined fractions, pour the extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K–D concentrator. Rinse the Erlenmeyer flask and column with 20–30 mL of methylene chloride to complete the quantitative transfer.

10.2.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction (Section 10.2.7). Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. At the proper rate of

distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL or other determined amount, remove the K–D apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. If the sample will be cleaned up, reserve the K–D apparatus for concentration of the cleaned up extract. Adjust the volume to 5 mL with methylene chloride and proceed to Section 11 for cleanup; otherwise, further concentrate the extract for GC/MS analysis per Section 10.2.9 or 10.2.10.

10.2.9 Micro Kuderna-Danish concentration—add another one or two clean boiling chips to the concentrator tube for each fraction and attach a two-ball micro-Snyder column. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65 °C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5–10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 1 mL or other determined amount, remove the K–D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of or methylene chloride. Adjust the final volume to 1.0 mL or a volume appropriate to the sensitivity desired (*e.g.,* to meet lower MDLs or for selected ion monitoring). Record the volume, stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to fluoropolymer-lined screw-cap vials and labeled base/neutral or acid fraction as appropriate. Mark the level of the extract on the vial so that solvent loss can be detected.

10.2.10 Nitrogen evaporation and solvent exchange—Extracts may be concentrated for analysis using nitrogen evaporation in place of micro K–D concentration (Section 10.2.9). Extracts that have been cleaned up using sulfur removal (Section 12.2) and are ready for analysis are exchanged into methylene chloride.

10.2.10.1 Transfer the vial containing the sample extract to the nitrogen evaporation (blowdown) device (Section 5.8). Lower the vial into the water bath and begin concentrating. If the more volatile analytes (Section 1.2) are to be concentrated, use room temperature for concentration; otherwise, a slightly elevated (*e.g.,* 30–45 °C) may be used. During the solvent evaporation process, keep the solvent level below the water level of the bath and do not allow the extract to become dry. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed. A large vortex in the solvent may cause analyte loss.

10.2.10.2 Extracts to be solvent exchanged—When the volume of the liquid is approximately 200 µL, add 2 to 3 mL of methylene chloride and continue concentrating to approximately 100 µL. Repeat the addition of solvent and concentrate once more. Adjust the final extract volume to be consistent with the volume extracted and the sensitivity desired.

10.2.10.3 For extracts that have been cleaned up by GPC and that are to be concentrated to a nominal volume of 1 mL, adjust the final volume to compensate the GPC loss. For a 50% GPC loss, concentrate the extract to 1/2000 of the volume extracted. For example, if the volume extracted is 950 mL, adjust the final volume to 0.48 mL. For extracts that have not been cleaned up by GPC and are to be concentrated to a nominal volume of 1.0 mL, adjust the final extract volume to 1/1000 of the volume extracted. For example, if the volume extracted is 950 mL, adjust the final extract volume to 0.95 mL.

Note: The difference in the volume fraction for an extract cleaned up by GPC accounts for the loss in GPC cleanup. Also, by preserving the ratio between the volume extracted and the final extract volume, the concentrations and detection limits do not need to be adjusted for differences in the volume extracted and the extract volume.

10.2.11 Transfer the concentrated extract to a vial with fluoropolymer-lined cap. Seal the vial and label with the sample number. Store in the dark at room temperature until ready for GC analysis. If GC analysis will not be performed on the same day, store the vial in the dark at ≤6 °C. Analyze the extract by GC/MS per the procedure in Section 12.

10.2.12 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to an appropriately sized graduated cylinder. For sample volumes on the order of 1000 mL, record the sample volume to the nearest 10 mL; for sample volumes on the order of 100 mL, record the volume to the nearest 1 mL. Sample volumes may also be determined by weighing the container before and after filling to the mark with water.

10.3 Continuous liquid/liquid extraction (CLLE).

Note: With CLLE, phenol, 2,4-dimethyl phenol, and some other analytes may be preferentially extracted into the base-neutral fraction. Determine an analyte in the fraction in which it is identified and quantified most reliably. Also, the short-chain phthalate esters (*e.g.,* dimethyl phthalate, diethyl phthalate) and some other compounds may hydrolyze during prolonged exposure to basic conditions required for continuous extraction, resulting in low recovery of these analytes. When these analytes are of interest, their recovery may be improved by performing the acid extraction first.

10.3.1 Use CLLE when experience with a sample from a given source indicates an emulsion problem, or when an emulsion is encountered during SFLLE. CLLE may be used for all samples, if desired.

10.3.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Check the pH of the sample with wide-range pH paper and adjust to pH 11–13 with sodium hydroxide solution. Transfer the sample to the continuous extractor. Pipet surrogate standard spiking solution (Section 6.8) into the sample. If the sample will be used for the LCS or MS or MSD, pipet the appropriate check sample concentrate (Section 8.2.1 or 8.3.2) into the extractor. Mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor.

10.3.3 Repeat the sample bottle rinse with an additional 50–100 mL portion of methylene chloride and add the rinse to the extractor.

10.3.4 Add a suitable volume of methylene chloride to the distilling flask (generally 200–500 mL), add sufficient reagent water to ensure proper operation, and extract for 18–24 hours. A shorter or longer extraction time may be used if all QC acceptance criteria are met. Test and, if necessary, adjust the pH of the water during the second or third hour of the extraction. After extraction, allow the apparatus to cool, then detach the distilling flask. Dry, concentrate, and seal the extract per Sections 10.2.6 through 10.2.11. See the note at Section 10.2.5 regarding combining extracts of the base/neutral and acid fractions.

10.3.5 Charge the distilling flask with methylene chloride and attach it to the continuous extractor. Carefully,

while stirring, adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Extract for 18–24 hours. A shorter or longer extraction time may be used if all QC acceptance criteria are met. Test and, if necessary, adjust the pH of the water during the second or third hour of the extraction. After extraction, allow the apparatus to cool, then detach the distilling flask. Dry, concentrate, and seal the extract per Sections 10.2.6 through 10.2.11. Determine the sample volume per Section 10.2.12.

11. Extract Cleanup

Note: Cleanup may not be necessary for relatively clean samples (*e.g.,* treated effluents, groundwater, drinking water). If particular circumstances require the use of a cleanup procedure, the laboratory may use any or all of the procedures below or any other appropriate procedure. Before using a cleanup procedure, the laboratory must demonstrate that the requirements of Section 8.1.2 can be met using the cleanup procedure as an integral part of this method.

11.1 Gel permeation chromatography (GPC).

11.1.1 Calibration.

11.1.1.1 Load the calibration solution (Section 6.12) into the sample loop.

11.1.1.2 Inject the calibration solution and record the signal from the detector. The elution pattern will be corn oil, bis(2-ethylhexyl) phthalate, pentachlorophenol, perylene, and sulfur.

11.1.1.3 Set the ''dump time'' to allow >85% removal of the corn oil and >85% collection of the phthalate.

11.1.1.4 Set the ''collect time'' to the peak minimum between perylene and sulfur.

11.1.1.5 Verify calibration with the calibration solution after every 20 or fewer extracts. Calibration is verified if the recovery of the pentachlorophenol is greater than 85%. If calibration is not verified, recalibrate using the calibration solution, and re-extract and clean up the preceding extracts using the calibrated GPC system.

11.1.2 Extract cleanup—GPC requires that the column not be overloaded. The column specified in this method is designed to handle a maximum of 0.5 g of high molecular weight material in a 5-mL extract. If the extract is known or expected to contain more than 0.5 g, the extract is split into fractions for GPC and the fractions are combined after elution from the column. The solids content of the extract may be obtained gravimetrically by evaporating the solvent from a 50-µL aliquot.

11.1.2.1 Filter the extract or load through the filter holder to remove particulates. Load the extract into the sample loop. The maximum capacity of the column is 0.5–1.0 g. If necessary, split the extract into multiple aliquots to prevent column overload.

11.1.2.2 Elute the extract using the calibration data determined in Section 11.1.1. Collect the eluate in the K–D apparatus reserved in Section 10.2.8.

11.1.3 Concentrate the cleaned up extract per Sections 10.2.8 and 10.2.9 or 10.2.10.

11.1.4 Rinse the sample loading tube thoroughly with methylene chloride between extracts to prepare for the next sample.

11.1.5 If a particularly dirty extract is encountered, run a methylene chloride blank through the system to check for carry-over.

11.2 Sulfur removal.

Note: Separate procedures using copper or TBA sulfite are provided in this section for sulfur removal. They may be used separately or in combination, if desired.

11.2.1 Removal with copper (Reference 17).

Note: If (1) an additional compound (Table 3) is to be determined; (2) sulfur is to be removed; (3) copper will be used for sulfur removal; and (4) a sulfur matrix is known or suspected to be present, the laboratory must demonstrate that the additional compound can be successfully extracted and treated with copper in the sulfur matrix. Some of the additional compounds (Table 3) are known not to be amenable to sulfur removal with copper (*e.g.* Atrazine and Diazinon).

11.2.1.1 Quantitatively transfer the extract from Section 10.2.8 to a 40- to 50-mL flask or bottle. If there is evidence of water in the concentrator tube after the transfer, rinse the tube with small portions of hexane:acetone (40:60) and add to the flask or bottle. Mark and set aside the concentrator tube for use in re-concentrating the extract.

11.2.1.2 Add 10–20 g of granular anhydrous sodium sulfate to the flask. Swirl to dry the extract.

11.2.1.3 Add activated copper (Section 6.13.1.4) and allow to stand for 30–60 minutes, swirling occasionally. If the copper does not remain bright, add more and swirl occasionally for another 30–60 minutes.

11.2.1.4 After drying and sulfur removal, quantitatively transfer the extract to a nitrogen-evaporation vial or tube and proceed to Section 10.2.10 for nitrogen evaporation and solvent exchange, taking care to leave the sodium sulfate and copper in the flask.

11.2.2 Removal with TBA sulfite.

11.2.2.1 Using small volumes of hexane, quantitatively transfer the extract to a 40- to 50-mL centrifuge tube with fluoropolymer-lined screw cap.

11.2.2.2 Add 1–2 mL of TBA sulfite reagent (Section 6.13.2.4), 2–3 mL of 2-propanol, and approximately 0.7 g of sodium sulfite (Section 6.13.2.2) crystals to the tube. Cap and shake for 1–2 minutes. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 0.5 g portions until a solid residue remains after repeated shaking.

11.2.2.3 Add 5–10 mL of reagent water and shake for 1–2 minutes. Centrifuge to settle the solids.

11.2.2.4 Quantitatively transfer the hexane (top) layer through a small funnel containing a few grams of granular anhydrous sodium sulfate to a nitrogen-evaporation vial or tube and proceed to Section 10.2.10 for nitrogen evaporation and solvent exchange.

12. Gas Chromatography/Mass Spectrometry

12.1 Establish the operating conditions in Table 4 or 5 for analysis of a base/neutral or acid extract, respectively. For analysis of a combined extract (Section 10.2.5, note), use the operating conditions in Table 4. Included in these tables are retention times and MDLs that can be achieved under these conditions. Examples of the separations achieved are shown in Figure 2 for the combined extract. Alternative columns or chromatographic conditions may be used if the requirements of Section 8.2 are met. Verify system performance per Section 13.

12.2 Analysis of a standard or extract.

12.2.1 Bring the standard or concentrated extract (Section 10.2.9 or 10.2.11) to room temperature and verify that any precipitate has redissolved. Verify the level on the extract and bring to the mark with solvent if required.

12.2.2 Add the internal standard solution (Section 6.9) to the extract. Mix thoroughly.

12.2.3 Inject an appropriate volume of the sample extract or standard solution using split, splitless, solvent purge, large-volume, or on-column injection. If the sample is injected manually the solvent-flush technique should be used. The injection volume depends upon the technique used and the ability to meet MDLs or reporting limits for regulatory compliance. Injected volumes must be the same for standards and sample extracts. Record the volume injected to two significant figures.

12.2.3.1 Start the GC column oven program upon injection. Start MS data collection after the solvent peak elutes. Stop data collection after benzo(ghi)perylene elutes for the base/neutral or combined fractions, or after pentachlorophenol elutes for the acid fraction. Return the column to the initial temperature for analysis of the next standard solution or extract.

12.2.3.2 If the concentration of any analyte of interest exceeds the calibration range, either extract and analyze a smaller sample volume, or dilute and analyze the diluted extract after bringing the concentrations of the internal standards to the levels in the undiluted extract.

12.2.4 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When standards and extracts are not being used for analyses, store them refrigerated at ≤6 °C protected from light in screw-cap vials equipped with un-pierced fluoropolymer-lined septa.

13. Performance tests

13.1 At the beginning of each 12-hour shift during which standards or extracts will be analyzed, perform the tests in Sections 13.2–13.7 to verify system performance. If DDT and/or endrin are to be determined, perform the decomposition test in Section 13.8. If an extract is concentrated for greater sensitivity (*e.g.,* by SIM), all tests must be performed at levels consistent with the reduced extract volume.

13.2 DFTPP—Inject the DFTPP standard (Section 6.10) and verify that the criteria for DFTPP in Section 7.2.1.1 and Table 9A (Reference 18) for a quadrupole MS, or Table 9B (Reference 19) for a time-of-flight MS, are met. It is not necessary to meet DFTPP criteria for SIM operation.

13.3 GC resolution—There must be a valley between benzo(b)fluoranthene and benzo(k)fluoranthene at m/z 252, and the height of the valley must not exceed 25 percent of the shorter of the two peaks.

13.4 Calibration verification—Verify calibration per Sections 7.3 and Table 6.

13.5 Peak tailing—Verify the tailing factor specifications are met per Section 7.2.1.1.

13.6 Laboratory control sample and blank—Analyze the extracts of the LCS and blank at the beginning of analyses of samples in the extraction batch (Section 3.1). The LCS must meet the requirements in Section 8.4, and the blank must meet the requirements in Section 8.5 before sample extracts may be analyzed.

13.7 Matrix spike/matrix spike duplicate—Analyze the background sample for the MS/MSD and the MS and MSD after the blank (Section 8.3.2). Results for the MS/MSD must meet the requirements in Section 8.3 before a result for an analyte in any unspiked sample in the batch may be reported or used for permitting or regulatory compliance purposes.

13.8 DDT/endrin decomposition test—If DDT and/or endrin analytes of interest, the DDT/endrin test (Section 8.8) must be performed and the QC acceptance criteria must be met before analyzing samples for DDT and/or endrin.

14. Qualitative Identification

14.1 Identification is accomplished by comparison of data from analysis of a sample or blank with data stored in the GC/MS data system (Sections 5.6.5 and 7.2.1.2, and Tables 4 and 5). Identification of an analyte is confirmed per Sections 14.1.1 through 14.1.4.

14.1.1 The signals for all characteristic m/z's stored in the data system for each analyte of interest must be present and must maximize within the same two consecutive scans.

14.1.2 Based on the relative retention time (RRT), the RRT for the analyte must be within ±0.06 of the RRT of the analyte in the calibration verification run at the beginning of the shift (Section 7.3 or 13.4). Relative retention time is used to establish the identification window because it compensates for small changes in the GC temperature program whereas the absolute retention time does not (see Section 6.9.3).

Note: RRT is a unitless quantity (see Sec. 20.2), although some procedures refer to ''RRT units'' in providing the specification for the agreement between the RRT values in the sample and the calibration verification or other standard.

14.1.3 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum, must agree within 50% to 200% (½ to 2 times) for all m/z's in the reference mass spectrum stored in the data system (Section 7.2.1.2), or from a reference library. For example, if a peak has an intensity of 20% relative to the base peak, the analyte is identified if the intensity of the peak in the sample is in the range of 10% to 40% of the base peak.

14.1.4 The m/z's present in the acquired mass spectrum for the sample that are not present in the reference mass spectrum must be accounted for by contaminant or background m/z's. A reference library may be helpful to identify and account for background or contaminant m/z's. If the acquired mass spectrum is contaminated, or if identification is ambiguous, an experienced spectrometrist (Section 1.7) must determine the presence or absence of the compound.

14.2 Structural isomers that have very similar mass spectra can be identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 50% of the height of the shorter of the two peaks. Otherwise, structural isomers are identified as isomeric pairs.

15. Calculations

15.1 When an analyte has been identified, quantitation of that analyte is based on the integrated abundance from the EICP of the primary characteristic m/z in Table 4 or 5. Calculate the concentration in the extract using the response factor (RF) determined in Section 7.2.2 and Equation 2. If the concentration of an analyte exceeds the calibration range, dilute the extract by the minimum amount to bring the concentration into the calibration range, and re-analyze the extract. Determine a dilution factor (DF) from the amount of the dilution. For example, if the extract is diluted by a factor of 2, DF = 2.

$$C_{ex}\ (\mu g/mL) = \frac{A_s \times I_{is}}{A_{is} \times RF}$$

Equation 2

Where:

C_{ex} = Concentration of the analyte in the extract, in µg/mL, and the other terms are as defined in Equation 1.

Calculate the concentration of the analyte in the sample using the concentration in the extract, the extract volume, the sample volume, and the dilution factor, per Equation 3:

$$C_s\ (\mu g/L) = \frac{C_{ex} \times V_{ex} \times DF}{V_s}$$ Equation 3

Where:

C_s = Concentration of the analyte in the sample

C_{ex} = Concentration of the analyte in the extract, in µg/mL

V_{ex} = Volume of extract (mL)

V_s = Volume of sample (L)

DF = Dilution factor

15.2 Reporting of results

As noted in Section 1.4.1, EPA has promulgated this method at 40 CFR part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described here are focused on such monitoring needs and may not be relevant to other uses of the method.

15.2.1 Report results for wastewater samples in µg/L without correction for recovery. (Other units may be used if required by in a permit.) Report all QC data with the sample results.

15.2.2 Reporting level

Unless otherwise specified in by a regulatory authority or in a discharge permit, results for analytes that meet the identification criteria are reported down to the concentration of the ML established by the laboratory through calibration of the instrument (see Section 7.3.2 and the glossary for the derivation of the ML). EPA considers the terms ''reporting limit,'' ''quantitation limit,'' and ''minimum level'' to be synonymous.

15.2.2.1 Report a result for each analyte in each sample, blank, or standard at or above the ML to 3 significant figures. Report a result for each analyte found in each sample below the ML as ''ML,'' or as required by the regulatory authority or permit. Results are reported without blank subtraction unless requested or required by a regulatory authority or in a permit. In this case, both the sample result and the blank results must be reported together.

15.2.2.2 In addition to reporting results for samples and blanks separately, the concentration of each analyte in a blank associated with the sample may be subtracted from the result for that sample, but only if requested or required by a regulatory authority or in a permit. In this case, both the sample result and the blank results must be reported together.

15.2.2.3 Report a result for an analyte found in a sample or extract that has been diluted at the least dilute level at which the area at the quantitation m/z is within the calibration range (*i.e.,* above the ML for the analyte) and the MS/MSD recovery and RPD are within their respective QC acceptance criteria (Table 6). This may require reporting results for some analytes from different analyses.

15.2.3 Results from tests performed with an analytical system that is not in control (*i.e.,* that does not meet acceptance criteria for all of QC tests in this method) must not be reported or otherwise used for permitting or regulatory compliance purposes, but do not relieve a discharger or permittee of reporting timely results. If the holding time would be exceeded for a re-analysis of the sample, the regulatory/control authority should be consulted for disposition.

16. Method Performance

16.1 The basic version of this method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5–1300 µg/L (Reference 2). Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

16.2 As noted in Sec. 1.1, this method was validated through an interlaboratory study conducted more than 29 years ago. However, the fundamental chemistry principles used in this method remain sound and continue to apply.

16.3 A chromatogram of the combined acid/base/neutral calibration standard is shown in Figure 2.

17. Pollution Prevention

17.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operations. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, the laboratory should use pollution prevention techniques to address waste generation. When wastes cannot be reduced at the source, the Agency recommends recycling as the next best option.

17.2 The analytes in this method are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards. This method utilizes significant quantities of methylene chloride. Laboratories are encouraged to recover and recycle this and other solvents during extract concentration.

17.3 For information about pollution prevention that may be applied to laboratories and research institutions, consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW., Washington, DC 20036, 202/872–4477.

18. Waste Management

18.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. An overview of requirements can be found in Environmental Management Guide for Small Laboratories (EPA 233–B–98–001).

18.2 Samples at pH <2, or pH >12 are hazardous and must be neutralized before being poured down a drain, or must be handled and disposed of as hazardous waste.

18.3 Many analytes in this method decompose above 500 °C. Low-level waste such as absorbent paper, tissues, and plastic gloves may be burned in an appropriate incinerator. Gross quantities of neat or highly concentrated solutions of toxic or hazardous chemicals should be packaged securely and disposed of through commercial or governmental channels that are capable of handling these types of wastes.

18.4 For further information on waste management, consult The Waste Management Manual for Laboratory Personnel and Less is Better-Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW., Washington, DC 20036, 202/872–4477.

19. References

1. ''Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants,'' U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1977, Revised April 1977.
2. ''EPA Method Study 30, Method 625, Base/Neutrals, Acids, and Pesticides,'' EPA 600/4–84–053, National Technical Information Service, PB84–206572, Springfield, Virginia 22161, June 1984.
3. 40 CFR part 136, appendix B.
4. Olynyk, P., Budde, W.L. and Eichelberger, J.W. ''Method Detection Limit for Methods 624 and 625,'' Unpublished report, May 14, 1980.
5. Annual Book of ASTM Standards, Volume 11.02, D3694–96, ''Standard Practices for Preparation of Sample Containers and for Preservation of Organic Constituents,'' American Society for Testing and Materials, Philadelphia.
6. Solutions to Analytical Chemistry Problems with Clean Water Act Methods, EPA 821–R–07–002, March 2007.
7. ''Carcinogens-Working With Carcinogens,'' Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77–206, August 1977.
8. ''OSHA Safety and Health Standards, General Industry,'' (29 CFR part 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).
9. ''Safety in Academic Chemistry Laboratories,'' American Chemical Society Publication, Committee on Chemical Safety, 7th Edition, 2003.
10. *http://en.wikipedia.org/wiki/Coefficient_of_determination* (accessed on 09/10/2013).
11. 40 CFR 136.6(b)(4)(x).
12. 40 CFR 136.6(b)(2)(i).
13. Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water (EPA–821–B–98–003) March 1999.
14. Provost, L.P. and Elder, R.S. ''Interpretation of Percent Recovery Data,'' American Laboratory, 15, 58–63 (1983). (The value 2.44 used in the equation in Section 8.3.3 is two times the value 1.22 derived in this report.)
15. ASTM Annual Book of Standards, Part 31, D3370–76. ''Standard Practices for Sampling Water,'' American Society for Testing and Materials, Philadelphia.
16. 40 CFR 136.3(a), Table IB, Chlorine—Total Residual.
17. ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples,'' EPA–600/8–80–038, U.S. Environmental Protection Agency, Health Effects Research Laboratory, Research Triangle Park, North Carolina.
18. Eichelberger, J.W., Harris, L.E., and Budde, W.L. ''Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry,'' Analytical Chemistry, 47, 995 (1975).
19. Letter of approval of acceptance criteria for DFTPP for time-of-flight mass spectrometers from William A. Telliard and Herb Brass of EPA to Jack Cochran of LECO Corporation, February 9, 2005.

20. Tables.

TABLE 1—NON PESTICIDE/PCB BASE/NEUTRAL EXTRACTABLES [1]

Analyte	CAS Registry	MDL [4]	ML [5]
Acenaphthene	83–32–9	1.9	5.7
Acenaphthylene	208–96–8	3.5	10.5
Anthracene	120–12–7	1.9	5.7
Benzidine [2]	92–87–5	44	132
Benzo(a)anthracene	56–55–3	7.8	23.4
Benzo(a)pyrene	50–32–8	2.5	7.5
Benzo(b)fluoranthene	205–99–2	4.8	14.4
Benzo(k)fluoranthene	207–08–9	2.5	7.5
Benzo(ghi)perylene	191–24–2	4.1	12.3
Benzyl butyl phthalate	85–68–7	2.5	7.5
bis(2-Chloroethoxy)methane	111–91–1	5.3	15.9
bis(2-Ethylhexyl)phthalate	117–81–7	2.5	7.5
bis(2-Chloroisopropyl) ether (2,2′-Oxybis(1-chloropropane))	108–60–1	5.7	17.1
4-Bromophenyl phenyl ether	101–55–3	1.9	5.7
2-Chloronaphthalene	91–58–7	1.9	5.7
4-Chlorophenyl phenyl ether	7005–72–3	4.2	12.6
Chrysene	218–01–9	2.5	7.5
Dibenz(a,h)anthracene	53–70–3	2.5	7.5
Di-*n*-butylphthalate	84–74–2	2.5	7.5
3,3′-Dichlorobenzidine	91–94–1	16.5	49.5
Diethyl phthalate	84–66–2	1.9	5.7
Dimethyl phthalate	131–11–3	1.6	4.8
2,4-Dinitrotoluene	121–14–2	5.7	17.1
2,6-Dinitrotoluene	606–20–2	1.9	5.7
Di-n-octylphthalate	117–84–0	2.5	7.5
Fluoranthene	206–44–0	2.2	6.6
Fluorene	86–73–7	1.9	5.7
Hexachlorobenzene	118–74–1	1.9	5.7
Hexachlorobutadiene	87–68–3	0.9	2.7
Hexachloroethane	67–72–1	1.6	4.8
Indeno(1,2,3-cd)pyrene	193–39–5	3.7	11.1
Isophorone	78–59–1	2.2	6.6
Naphthalene	91–20–3	1.6	4.8
Nitrobenzene	98–95–3	1.9	5.7
N-Nitrosodi-*n*-propylamine [3]	621–64–7	—	—
Phenanthrene	85–01–8	5.4	16.2
Pyrene	129–00–0	1.9	5.7
1,2,4-Trichlorobenzene	120–82–1	1.9	5.7

[1] All analytes in this table are Priority Pollutants (40 CFR part 423, appendix A).

[2] Included for tailing factor testing.
[3] See Section 1.2.
[4] MDL values from the 1984 promulgated version of Method 624.
[5] ML = Minimum Level—see Glossary for definition and derivation.

TABLE 2—ACID EXTRACTABLES [1]

Analyte	CAS Registry	MDL [3]	ML [4]
4-Chloro-3-methylphenol	59–50–7	3.0	9.0
2-Chlorophenol	95–57–8	3.3	9.9
2,4-Dichlorophenol	120–83–2	2.7	8.1
2,4-Dimethylphenol	105–67–9	2.7	8.1
2,4-Dinitrophenol	51–28–5	42	126
2-Methyl-4,6-dinitrophenol	534–52–1	24	72
2-Nitrophenol	88–75–5	3.6	10.8
4-Nitrophenol	100–02–7	2.4	7.2
Pentachlorophenol [2]	87–86–5	3.6	10.8
Phenol	108–95–2	1.5	4.5
2,4,6-Trichlorophenol	88–06–2	2.7	8.1

[1] All analytes in this table are Priority Pollutants (40 CFR part 423, appendix A).
[2] See Section 1.2; included for tailing factor testing.
[3] MDL values from the 1984 promulgated version of Method 624.
[4] ML = Minimum Level—see Glossary for definition and derivation.

TABLE 3—ADDITIONAL EXTRACTABLE ANALYTES [1 2]

Analyte	CAS Registry	MDL [6]	ML [7]
Acetophenone	98–86–2		
2-Acetylaminofluorene	53–96–3		
1-Acetyl-2-thiourea	591–08–2		
Alachlor	15972–60–8		
Aldrin [3]	309–00–2	1.9	5.7
Ametryn	834–12–8		
2-Aminoanthraquinone	117–79–3		
Aminoazobenzene	60–09–3		
4-Aminobiphenyl	92–67–1		
3-Amino-9-ethylcarbazole	132–32–1		
Anilazine	101–05–3		
Aniline	62–53–3		
o-Anisidine	90–04–0		
Aramite	140–57–8		
Atraton	1610–17–9		
Atrazine	1912–24–9		
Azinphos-methyl	86–50–0		
Barban	101–27–9		
Benzanthrone	82–05–3		
Benzenethiol	108–98–5		
Benzidine [3 4]	92–87–5	44	132
Benzoic acid	65–85–0		
2,3-Benzofluorene	243–17–4		
p-Benzoquinone	106–51–4		
Benzyl alcohol	100–51–6		
alpha-BHC [3 4]	319–84–6		
beta-BHC [3]	319–85–7	3.1	9.3
gamma-BHC (Lindane) [3 4]	58–89–8	4.2	12.6
delta-BHC [3]	319–86–8		
Biphenyl	92–52–4		
Bromacil	314–40–9		
2-Bromochlorobenzene	694–80–4		
3-Bromochlorobenzene	108–39–2		
Bromoxynil	1689–84–5		
Butachlor	2318–4669		
Butylate	2008–41–5		
n-C10 (*n*-decane)	124–18–5		
n-C12 (*n*-undecane)	112–40–2		
n-C14 (*n*-tetradecane)	629–59–4		
n-C16 (*n*-hexadecane)	544–76–3		
n-C18 (*n*-octadecane)	593–45–3		
n-C20 (*n*-eicosane)	112–95–8		
n-C22 (*n*-docosane)	629–97–0		
n-C24 (*n*-tetracosane)	646–31–1		
n-C26 (*n*-hexacosane)	630–01–3		
n-C28 (*n*-octacosane)	630–02–4		
n-C30 (*n*-triacontane)	638–68–6		

TABLE 3—ADDITIONAL EXTRACTABLE ANALYTES [1 2]—Continued

Analyte	CAS Registry	MDL [6]	ML [7]
Captafol	2425–06–1		
Captan	133–06–2		
Carbaryl	63–25–2		
Carbazole	86–74–8		
Carbofuran	1563–66–2		
Carboxin	5234–68–4		
Carbophenothion	786–19–6		
Chlordane[3 5]	57–74–9		
bis(2-Chloroethyl) ether [3 4]	111–44–4	5.7	17.1
Chloroneb	2675–77–6		
4-Chloroaniline	106–47–8		
Chlorobenzilate	510–15–6		
Chlorfenvinphos	470–90–6		
4-Chloro-2-methylaniline	95–69–2		
3-(Chloromethyl)pyridine hydrochloride	6959–48–4		
4-Chloro-2-nitroaniline	89–63–4		
Chlorpropham	101–21–3		
Chlorothalonil	1897–45–6		
1-Chloronaphthalene	90–13–1		
3-Chloronitribenzene	121–73–3		
4-Chloro-1,2-phenylenediamine	95–83–0		
4-Chloro-1,3-phenylenediamine	5131–60–2		
2-Chlorobiphenyl	2051–60–7		
Chlorpyrifos	2921–88–2		
Coumaphos	56–72–4		
m+p-Cresol	65794–96–9		
o-Cresol	95–48–7		
p-Cresidine	120–71–8		
Crotoxyphos	7700–17–6		
2-Cyclohexyl-4,6-dinitro-phenol	131–89–5		
Cyanazine	21725–46–2		
Cycloate	1134–23–2		
p-Cymene	99–87–6		
Dacthal (DCPA)	1861–32–1		
4,4′-DDD [3]	72–54–8	2.8	8.4
4,4′-DDE [3]	72–55–9	5.6	16.8
4,4′-DDT [3]	50–29–3	4.7	14.1
Demeton-O	298–03–3		
Demeton-S	126–75–0		
Diallate (*cis* or *trans*)	2303–16–4		
2,4-Diaminotoluene	95–80–7		
Diazinon	333–41–5		
Dibenz(a,j)acridine	224–42–0		
Dibenzofuran	132–64–9		
Dibenzo(a,e)pyrene	192–65–4		
Dibenzothiophene	132–65–0		
1,2-Dibromo-3-chloropropane	96–12–8		
3,5-Dibromo-4-hydroxybenzonitrile	1689–84–5		
2,6-Di-tert-butyl-p-benzoquinone	719–22–2		
Dichlone	117–80–6		
2,3-Dichloroaniline	608–27–5		
2,3-Dichlorobiphenyl	16605–91–7		
2,6-Dichloro-4-nitroaniline	99–30–9		
2,3-Dichloronitrobenzene	3209–22–1		
1,3-Dichloro-2-propanol	96–23–1		
2,6-Dichlorophenol	120–83–2		
Dichlorvos	62–73–7		
Dicrotophos	141–66–2		
Dieldrin [3]	60–57–1	2.5	7.5
1,2:3,4-Diepoxybutane	1464–53–5		
Di(2-ethylhexyl) adipate	103–23–1		
Diethylstilbestrol	56–53–1		
Diethyl sulfate	64–67–5		
Dilantin (5,5-Diphenylhydantoin)	57–41–0		
Dimethoate	60–51–5		
3,3′-Dimethoxybenzidine	119–90–4		
Dimethylaminoazobenzene	60–11–7		
7,12-Dimethylbenz(a)anthracene	57–97–6		
3,3′-Dimethylbenzidine	119–93–7		
N,N-Dimethylformamide	68–12–2		
3,6-Dimethylphenathrene	1576–67–6		
alpha, alpha-Dimethylphenethylamine	122–09–8		

TABLE 3—ADDITIONAL EXTRACTABLE ANALYTES [1 2]—Continued

Analyte	CAS Registry	MDL [6]	ML [7]
Dimethyl sulfone	67–71–0		
1,2-Dinitrobenzene	528–29–0		
1,3-Dinitrobenzene	99–65–0		
1,4-Dinitrobenzene	100–25–4		
Dinocap	39300–45–3		
Dinoseb	88–85–7		
Diphenylamine	122–39–4		
Diphenyl ether	101–84–8		
1,2-Diphenylhydrazine	122–66–7		
Diphenamid	957–51–7		
Diphenyldisulfide	882–33–7		
Disulfoton	298–04–4		
Disulfoton sulfoxide	2497–07–6		
Disulfoton sulfone	2497–06–5		
Endosulfan I [3 4]	959–98–8		
Endosulfan II [3 4]	33213–65–9		
Endosulfan sulfate [3]	1031–07–8	5.6	16.8
Endrin [3 4]	72–20–8		
Endrin aldehyde [3 4]	7421–93–4		
Endrin ketone [3 4]	53494–70–5		
EPN	2104–64–5		
EPTC	759–94–4		
Ethion	563–12–2		
Ethoprop	13194–48–4		
Ethyl carbamate	51–79–6		
Ethyl methanesulfonate	65–50–0		
Ethylenethiourea	96–45–7		
Etridiazole	2593–15–9		
Ethynylestradiol-3-methyl ether	72–33–3		
Famphur	52–85–7		
Fenamiphos	22224–92–6		
Fenarimol	60168–88–9		
Fensulfothion	115–90–2		
Fenthion	55–38–9		
Fluchloralin	33245–39–5		
Fluridone	59756–60–4		
Heptachlor [3]	76–44–8	1.9	5.7
Heptachlor epoxide [3]	1024–57–3	2.2	6.6
2,2′,3,3′,4,4′,6-Heptachlorobiphenyl	52663–71–5		
2,2′,4,4′,5′,6-Hexachlorobiphenyl	60145–22–4		
Hexachlorocyclopentadiene [3 4]	77–47–4		
Hexachlorophene	70–30–4		
Hexachloropropene	1888–71–7		
Hexamethylphosphoramide	680–31–9		
Hexanoic acid	142–62–1		
Hexazinone	51235–04–2		
Hydroquinone	123–31–9		
Isodrin	465–73–6		
2-Isopropylnapthalene	2027–17–0		
Isosafrole	120–58–1		
Kepone	143–50–0		
Leptophos	21609–90–5		
Longifolene	475–20–7		
Malachite green	569–64–2		
Malathion	121–75–5		
Maleic anhydride	108–31–6		
Merphos	150–50–5		
Mestranol	72–33–3		
Methapyrilene	91–80–5		
Methoxychlor	72–43–5		
2-Methylbenzothioazole	120–75–2		
3-Methylcholanthrene	56–49–5		
4,4′-Methylenebis(2-chloroaniline)	101–14–4		
4,4′-Methylenebis(N,N-dimethylaniline)	101–61–1		
4,5-Methylenephenanthrene	203–64–5		
1-Methylfluorene	1730–37–6		
Methyl methanesulfonate	66–27–3		
2-Methylnaphthalene	91–57–6		
Methylparaoxon	950–35–6		
Methyl parathion	298–00–0		
1-Methylphenanthrene	832–69–9		
2-(Methylthio)benzothiazole	615–22–5		

TABLE 3—ADDITIONAL EXTRACTABLE ANALYTES [1 2]—Continued

Analyte	CAS Registry	MDL [6]	ML [7]
Metolachlor	5218–45–2		
Metribuzin	21087–64–9		
Mevinphos	7786–34–7		
Mexacarbate	315–18–4		
MGK 264	113–48–4		
Mirex	2385–85–5		
Molinate	2212–67–1		
Monocrotophos	6923–22–4		
Naled	300–76–5		
Napropamide	15299–99–7		
1,4-Naphthoquinone	130–15–4		
1-Naphthylamine	134–32–7		
2-Naphthylamine	91–59–8		
1,5-Naphthalenediamine	2243–62–1		
Nicotine	54–11–5		
5-Nitroacenaphthene	602–87–9		
2-Nitroaniline	88–74–4		
3-Nitroaniline	99–09–2		
4-Nitroaniline	100–01–6		
5-Nitro-*o*-anisidine	99–59–2		
4-Nitrobiphenyl	92–93–3		
Nitrofen	1836–75–5		
5-Nitro-*o*-toluidine	99–55–8		
Nitroquinoline-1-oxide	56–57–5		
N-Nitrosodi-*n*-butylamine [4]	924–16–3		
N-Nitrosodiethylamine [4]	55–18–5		
N-Nitrosodimethylamine [3 4]	62–75–9		
N-Nitrosodiphenylamine [3 4]	86–30–6		
N-Nitrosomethylethylamine [4]	10595–95–6		
N-Nitrosomethylphenylamine [4]	614–00–6		
N-Nitrosomorpholine [4]	59–89–2		
N-Nitrosopiperidine [4]	100–75–5		
N-Nitrosopyrrolidine [4]	930–55–2		
trans-Nonachlor	39765–80–5		
Norflurazon	27314–13–2		
2,2′,3,3′,4,5′,6,6′-Octachlorobiphenyl	40186–71–8		
Octamethyl pyrophosphoramide	152–16–9		
4,4'-Oxydianiline	101–80–4		
Parathion	56–38–2		
PCB–1016 [3 5]	12674–11–2		
PCB–1221 [3 5]	11104–28–2	30	90
PCB–1232 [3 5]	11141–16–5		
PCB–1242 [3 5]	53469–21–9		
PCB–1248 [3 5]	12672–29–6		
PCB–1254 [3 5]	11097–69–1	36	108
PCB–1260 [3 5]	11098–82–5		
PCB–1268 [3 5]	11100–14–4		
Pebulate	1114–71–2		
Pentachlorobenzene	608–93–5		
Pentachloronitrobenzene	82–68–8		
2,2′,3,4′,6-Pentachlorobiphenyl	68194–05–8		
Pentachloroethane	76–01–7		
Pentamethylbenzene	700–12–9		
Perylene	198–55–0		
Phenacetin	62–44–2		
cis-Permethrin	61949–76–6		
trans-Permethrin	61949–77–7		
Phenobarbital	50–06–6		
Phenothiazene	92–84–2		
1,4-Phenylenediamine	624–18–0		
1-Phenylnaphthalene	605–02–7		
2-Phenylnaphthalene	612–94–2		
Phorate	298–02–2		
Phosalone	2310–18–0		
Phosmet	732–11–6		
Phosphamidon	13171–21–6		
Phthalic anhydride	85–44–9		
alpha-Picoline (2-Methylpyridine)	109–06–8		
Piperonyl sulfoxide	120–62–7		
Prometon	1610–18–0		
Prometryn	7287–19–6		
Pronamide	23950–58–5		

TABLE 3—ADDITIONAL EXTRACTABLE ANALYTES [1] [2]—Continued

Analyte	CAS Registry	MDL [6]	ML [7]
Propachlor	1918–16–7		
Propazine	139–40–2		
Propylthiouracil	51–52–5		
Pyridine	110–86–1		
Resorcinol (1,3-Benzenediol)	108–46–3		
Safrole	94–59–7		
Simazine	122–34–9		
Simetryn	1014–70–6		
Squalene	7683–64–9		
Stirofos	22248–79–9		
Strychnine	57–24–9		
Styrene	100–42–5		
Sulfallate	95–06–7		
Tebuthiuron	34014–18–1		
Terbacil	5902–51–2		
Terbufos	13071–79–9		
Terbutryn	886–50–0		
alpha-Terpineol	98–55–5		
1,2,4,5-Tetrachlorobenzene	95–94–3		
2,2′,4,4′-Tetrachlorobiphenyl	2437–79–8		
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	1746–01–6		
2,3,4,6-Tetrachlorophenol	58–90–2		
Tetrachlorvinphos	22248–79–9		
Tetraethyl dithiopyrophosphate	3689–24–5		
Tetraethyl pyrophosphate	107–49–3		
Thianaphthene (2,3-Benzothiophene)	95–15–8		
Thioacetamide	62–55–5		
Thionazin	297–97–2		
Thiophenol (Benzenethiol)	108–98–5		
Thioxanthone	492–22–8		
Toluene-1,3-diisocyanate	26471–62–5		
Toluene-2,4-diisocyanate	584–84–9		
o-Toluidine	95–53–4		
Toxaphene [3] [5]	8001–35–2		
Triadimefon	43121–43–3		
1,2,3-Trichlorobenzene	87–61–6		
2,4,5-Trichlorobiphenyl	15862–07–4		
2,3,6-Trichlorophenol	933–75–5		
2,4,5-Trichlorophenol	95–95–4		
Tricyclazole	41814–78–2		
Trifluralin	1582–09–8		
1,2,3-Trimethoxybenzene	634–36–6		
2,4,5-Trimethylaniline	137–17–7		
Trimethyl phosphate	512–56–1		
Triphenylene	217–59–4		
Tripropyleneglycolmethyl ether	20324–33–8		
1,3,5-Trinitrobenzene	99–35–4		
Tris(2,3-dibromopropyl) phosphate	126–72–7		
Tri-*p*-tolyl phosphate	78–32–0		
O,O,O-Triethyl phosphorothioate	126–68–1		
Trithiane	291–29–4		
Vernolate	1929–77–7		

[1] Compounds that have been demonstrated amenable to extraction and gas chromatography.
[2] Determine each analyte in the fraction that gives the most accurate result.
[3] Priority Pollutant (40 CFR part 423, appendix A).
[4] See Section 1.2.
[5] These compounds are mixtures of various isomers.
[6] MDL values from the 1984 promulgated version of Method 624.
[7] ML = Minimum Level—see Glossary for definition and derivation.

TABLE 4—CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC M/Z'S FOR BASE/NEUTRAL EXTRACTABLES

Analyte	Retention time (sec) [1]	Characteristic m/z's					
		Electron impact ionization			Chemical ionization		
		Primary	Second	Second	Methane	Methane	Methane
N-Nitrosodimethylamine	385	42	74	44			
bis(2-Chloroethyl) ether	704	93	63	95	63	107	109
bis(2-Chloroisopropyl) ether	799	45	77	79	77	135	137
Hexachloroethane	823	117	201	199	199	201	203

TABLE 4—CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC M/Z'S FOR BASE/NEUTRAL EXTRACTABLES—Continued

Analyte	Retention time (sec) [1]	Characteristic m/z's					
		Electron impact ionization			Chemical ionization		
		Primary	Second	Second	Methane	Methane	Methane
N-Nitrosodi-*n*-propylamine	830	130	42	101			
Nitrobenzene	849	77	123	65	124	152	164
Isophorone	889	82	95	138	139	167	178
bis(2-Chloroethoxy) methane	939	93	95	123	65	107	137
1,2,4-Trichlorobenzene	958	180	182	145	181	183	209
Naphthalene	967	128	129	127	129	157	169
Hexachlorobutadiene	1006	225	223	227	223	225	227
Hexachlorocyclopentadiene	1142	237	235	272	235	237	239
2-Chloronaphthalene	1200	162	164	127	163	191	203
Acenaphthylene	1247	152	151	153	152	153	181
Dimethyl phthalate	1273	163	194	164	151	163	164
2,6-Dinitrotoluene	1300	165	89	121	183	211	223
Acenaphthene	1304	154	153	152	154	155	183
2,4-Dinitrotoluene	1364	165	63	182	183	211	223
Fluorene	1401	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	1409	204	206	141			
Diethyl phthalate	1414	149	177	150	177	223	251
N-Nitrosodiphenylamine	1464	169	168	167	169	170	198
4-Bromophenyl phenyl ether	1498	248	250	141	249	251	277
alpha-BHC	1514	183	181	109			
Hexachlorobenzene	1522	284	142	249	284	286	288
beta-BHC	1544	183	181	109			
gamma-BHC	1557	181	183	109			
Phenanthrene	1583	178	179	176	178	179	207
Anthracene	1592	178	179	176	178	179	207
delta-BHC	1599	183	109	181			
Heptachlor	1683	100	272	274			
Di-*n*-butyl phthalate	1723	149	150	104	149	205	279
Aldrin	1753	66	263	220			
Fluoranthene	1817	202	101	100	203	231	243
Heptachlor epoxide	1820	353	355	351			
gamma-Chlordane	1834	373	375	377			
Pyrene	1852	202	101	100	203	231	243
Benzidine [2]	1853	184	92	185	185	213	225
alpha-Chlordane	1854	373	375	377			
Endosulfan I	1855	237	339	341			
4,4′-DDE	1892	246	248	176			
Dieldrin	1907	79	263	279			
Endrin	1935	81	263	82			
Endosulfan II	2014	237	339	341			
4,4′-DDD	2019	235	237	165			
Endrin aldehyde	2031	67	345	250			
Butyl benzyl phthalate	2060	149	91	206	149	299	327
Endosulfan sulfate	2068	272	387	422			
4,4′-DDT	2073	235	237	165			
Chrysene	2083	228	226	229	228	229	257
3,3′-Dichlorobenzidine	2086	252	254	126			
Benzo(a)anthracene	2090	228	229	226	228	229	257
bis(2-Ethylhexyl) phthalate	2124	149	167	279	149		
Di-*n*-octyl phthalate	2240	149	43	57			
Benzo(b)fluoranthene	2286	252	253	125	252	253	281
Benzo(k)fluoranthene	2293	252	253	125	252	253	281
Benzo(a)pyrene	2350	252	253	125	252	253	281
Indeno(1,2,3-cd) pyrene	2650	276	138	277	276	277	305
Dibenz(a,h)anthracene	2660	278	139	279	278	279	307
Benzo(ghi)perylene	2750	276	138	277	276	277	305
Toxaphene		159	231	233			
PCB 1016		224	260	294			
PCB 1221		190	224	260			
PCB 1232		190	224	260			
PCB 1242		224	260	294			
PCB 1248		294	330	262			
PCB 1254		294	330	362			
PCB 1260		330	362	394			

[1] Column: 30 m × 0.25 mm ID; 94% methyl, 5% phenyl, 1% vinyl bonded phase fused silica capillary.
Conditions: 5 min at 30 °C; 30–280 at 8 °C per min; isothermal at 280 °C until benzo(ghi)perylene elutes.
Gas velocity: 30 cm/sec at 30 °C (at constant pressure).
[2] See Section 1.2; included for tailing factor testing.

TABLE 5—CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC M/Z'S FOR ACID EXTRACTABLES

Analyte	Retention time (sec) [1]	Characteristic m/z's					
		Electron impact ionization			Chemical ionization		
		Primary	Second	Second	Methane	Methane	Methane
2-Chlorophenol	705	128	64	130	129	131	157
Phenol	700	94	65	66	95	123	135
2-Nitrophenol	900	139	65	109	140	168	122
2,4-Dimethylphenol	924	122	107	121	123	151	163
2,4-Dichlorophenol	947	162	164	98	163	165	167
4-Chloro-3-methylphenol	1091	142	107	144	143	171	183
2,4,6-Trichlorophenol	1165	196	198	200	197	199	201
2,4-Dinitrophenol	1325	184	63	154	185	213	225
4-Nitrophenol	1354	65	139	109	140	168	122
2-Methyl-4,6-dinitrophenol	1435	198	182	77	199	227	239
Pentachlorophenol	1561	266	264	268	267	265	269

Column: 30 m × 0.25 mm ID; 94% methyl, 5% phenyl, 1% vinyl bonded phase fused silica capillary.
Conditions: 5 min at 30 °C; 30–250 at 8 °C per min; isothermal at 280 °C until pentachlorophenol elutes.
Gas velocity: 30 cm/sec at 30 °C (at constant pressure).

TABLE 6—QC ACCEPTANCE CRITERIA—METHOD 625 [1]

Analyte	Range for Q (%) [2]	Limit for s (%) [3]	Range for $\bar{X}$ (%) [3]	Range for P, P_s (%) [3]	Limit for RPD (%)
Acenaphthene	70–130	29	60–132	47–145	48
Acenaphthylene	60–130	45	54–126	33–145	74
Aldrin	7–152	39	7–152	D–166	81
Anthracene	58–130	40	43–120	27–133	66
Benzo(a)anthracene	42–133	32	42–133	33–143	53
Benzo(b)fluoranthene	42–140	43	42–140	24–159	71
Benzo(k)fluoranthene	25–146	38	25–146	11–162	63
Benzo(a)pyrene	32–148	43	32–148	17–163	72
Benzo(ghi)perylene	13–195	61	D–195	D–219	97
Benzyl butyl phthalate	43–140	36	D–140	D–152	60
beta-BHC	42–131	37	42–131	24–149	61
delta-BHC	D–130	77	D–120	D–120	129
bis(2-Chloroethyl)ether	52–130	65	43–126	12–158	108
bis(2-Chloroethoxy)methane	52–164	32	49–165	33–184	54
bis(2-Chloroisopropyl) ether	63–139	46	63–139	36–166	76
bis(2-Ethylhexyl) phthalate	43–137	50	29–137	8–158	82
4-Bromophenyl phenyl ether	70–130	26	65–120	53–127	43
2-Chloronaphthalene	70–130	15	65–120	60–120	24
4-Chlorophenyl phenyl ether	57–145	36	38–145	25–158	61
Chrysene	44–140	53	44–140	17–168	87
4,4′-DDD	D–135	56	D–135	D–145	93
4,4′-DDE	19–130	46	19–120	4–136	77
4,4′-DDT	D–171	81	D–171	D–203	135
Dibenz(a,h)anthracene	13–200	75	D–200	D–227	126
Di-*n*-butyl phthalate	52–130	28	8–120	1–120	47
3,3′-Dichlorobenzidine	18–213	65	8–213	D–262	108
Dieldrin	70–130	38	44–119	29–136	62
Diethyl phthalate	47–130	60	D–120	D–120	100
Dimethyl phthalate	50–130	110	D–120	D–120	183
2,4-Dinitrotoluene	53–130	25	48–127	39–139	42
2,6-Dinitrotoluene	68–137	29	68–137	50–158	48
Di-*n*-octyl phthalate	21–132	42	19–132	4–146	69
Endosulfan sulfate	D–130	42	D–120	D–120	70
Endrin aldehyde	D–189	45	D–189	D–209	75
Fluoranthene	47–130	40	43–121	26–137	66
Fluorene	70–130	23	70–120	59–121	38
Heptachlor	D–172	44	D–172	D–192	74
Heptachlor epoxide	70–130	61	71–120	26–155	101
Hexachlorobenzene	38–142	33	8–142	D–152	55
Hexachlorobutadiene	68–130	38	38–120	24–120	62
Hexachloroethane	55–130	32	55–120	40–120	52
Indeno(1,2,3-cd)pyrene	13–151	60	D–151	D–171	99
Isophorone	52–180	56	47–180	21–196	93
Naphthalene	70–130	39	36–120	21–133	65
Nitrobenzene	54–158	37	54–158	35–180	62
N-Nitrosodi-*n*-propylamine	59–170	52	14–198	D–230	87
PCB–1260	19–130	77	19–130	D–164	128

TABLE 6—QC ACCEPTANCE CRITERIA—METHOD 625 [1]—Continued

Analyte	Range for Q (%) [2]	Limit for s (%) [3]	Range for $\bar{X}$ (%) [3]	Range for P, P_s (%) [3]	Limit for RPD (%)
Phenanthrene	67–130	24	65–120	54–120	39
Pyrene	70–130	30	70–120	52–120	49
1,2,4-Trichlorobenzene	61–130	30	57–130	44–142	50
4-Chloro-3-methylphenol	68–130	44	41–128	22–147	73
2-Chlorophenol	55–130	37	36–120	23–134	61
2,4-Dichlorophenol	64–130	30	53–122	39–135	50
2,4-Dimethylphenol	58–130	35	42–120	32–120	58
2,4-Dinitrophenol	39–173	79	D–173	D–191	132
2-Methyl-4,6-dinitrophenol	56–130	122	53–130	D–181	203
2-Nitrophenol	61–163	33	45–167	29–182	55
4-Nitrophenol	35–130	79	13–129	D–132	131
Pentachlorophenol	42–152	52	38–152	14–176	86
Phenol	48–130	39	17–120	5–120	64
2,4,6-Trichlorophenol	69–130	35	52–129	37–144	58

[1] Acceptance criteria are based upon method performance data in Table 7 and from EPA Method 1625. Where necessary, limits for recovery have been broadened to assure applicability to concentrations below those used to develop Table 7.
[2] Test concentration = 100 µg/mL.
[3] Test concentration = 100 µg/L.
Q = Calibration verification (Sections 7.3.1 and 13.4).
s = Standard deviation for four recovery measurements in the DOC test (Section 8.2.4).
$\bar{X}$ = Average recovery for four recovery measurements in the DOC test (Section 8.2.4).
P, Ps = MS/MSD recovery (Section 8.3.2, Section 8.4.2).
RPD = MS/MSD relative percent difference (RPD; Section 8.3.3).
D = Detected; result must be greater than zero.

TABLE 7—PRECISION AND RECOVERY AS FUNCTIONS OF CONCENTRATION—METHOD 625 [1]

Analyte	Recovery, X′ (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S′ (µg/L)
Acenaphthene	0.96C+0.19	0.15 $\bar{X}$ − 0.12	0.21 $\bar{X}$ − 0.67
Acenaphthylene	0.89C+0.74	0.24 $\bar{X}$ − 1.06	0.26 $\bar{X}$ − 0.54
Aldrin	0.78C+1.66	0.27 $\bar{X}$ − 1.28	0.43 $\bar{X}$ +1.13
Anthracene	0.80C+0.68	0.21 $\bar{X}$ − 0.32	0.27 $\bar{X}$ − 0.64
Benzo(a)anthracene	0.88C − 0.60	0.15 $\bar{X}$ +0.93	0.26 $\bar{X}$ − 0.28
Benzo(b)fluoranthene	0.93C − 1.80	0.22 $\bar{X}$ +0.43	0.29 $\bar{X}$ +0.96
Benzo(k)fluoranthene	0.87C − 1.56	0.19 $\bar{X}$ +1.03	0.35 $\bar{X}$ +0.40
Benzo(a)pyrene	0.90C − 0.13	0.22 $\bar{X}$ +0.48	0.32 $\bar{X}$ +1.35
Benzo(ghi)perylene	0.98C − 0.86	0.29 $\bar{X}$ +2.40	0.51 $\bar{X}$ − 0.44
Benzyl butyl phthalate	0.66C − 1.68	0.18 $\bar{X}$ +0.94	0.53 $\bar{X}$ +0.92
beta-BHC	0.87C − 0.94	0.20 $\bar{X}$ − 0.58	0.30 $\bar{X}$ − 1.94
delta-BHC	0.29C − 1.09	0.34 $\bar{X}$ +0.86	0.93 $\bar{X}$ − 0.17
bis(2-Chloroethyl)ether	0.86C − 1.54	0.35 $\bar{X}$ − 0.99	0.35 $\bar{X}$ +0.10
bis(2-Chloroethoxy)methane	1.12C − 5.04	0.16 $\bar{X}$ +1.34	0.26 $\bar{X}$ +2.01
bis(2-Chloroisopropyl)ether	1.03C − 2.31	0.24 $\bar{X}$ +0.28	0.25 $\bar{X}$ +1.04
bis(2-Ethylhexyl)phthalate	0.84C − 1.18	0.26 $\bar{X}$ +0.73	0.36 $\bar{X}$ +0.67
4-Bromophenyl phenyl ether	0.91C − 1.34	0.13 $\bar{X}$ +0.66	0.16 $\bar{X}$ +0.66
2-Chloronaphthalene	0.89C+0.01	0.07 $\bar{X}$ +0.52	0.13 $\bar{X}$ +0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20 $\bar{X}$ − 0.94	0.30 $\bar{X}$ − 0.46
Chrysene	0.93C − 1.00	0.28 $\bar{X}$ +0.13	0.33 $\bar{X}$ − 0.09
4,4′-DDD	0.56C − 0.40	0.29 $\bar{X}$ − 0.32	0.66 $\bar{X}$ − 0.96
4,4′-DDE	0.70C − 0.54	0.26 $\bar{X}$ − 1.17	0.39 $\bar{X}$ − 1.04
4,4′-DDT	0.79C − 3.28	0.42 $\bar{X}$ +0.19	0.65 $\bar{X}$ − 0.58
Dibenz(a,h)anthracene	0.88C+4.72	0.30 $\bar{X}$ +8.51	0.59 $\bar{X}$ +0.25
Di-*n*-butyl phthalate	0.59C+0.71	0.13 $\bar{X}$ +1.16	0.39 $\bar{X}$ +0.60
3,3′-Dichlorobenzidine	1.23C − 12.65	0.28 $\bar{X}$ +7.33	0.47 $\bar{X}$ +3.45
Dieldrin	0.82C − 0.16	0.20 $\bar{X}$ − 0.16	0.26 $\bar{X}$ − 0.07
Diethyl phthalate	0.43C+1.00	0.28 $\bar{X}$ +1.44	0.52 $\bar{X}$ +0.22
Dimethyl phthalate	0.20C+1.03	0.54 $\bar{X}$ +0.19	1.05 $\bar{X}$ − 0.92
2,4-Dinitrotoluene	0.92C − 4.81	0.12 $\bar{X}$ +1.06	0.21 $\bar{X}$ +1.50
2,6-Dinitrotoluene	1.06C − 3.60	0.14 $\bar{X}$ +1.26	0.19 $\bar{X}$ +0.35
Di-*n*-octyl phthalate	0.76C − 0.79	0.21 $\bar{X}$ +1.19	0.37 $\bar{X}$ +1.19
Endosulfan sulfate	0.39C+0.41	0.12 $\bar{X}$ +2.47	0.63 $\bar{X}$ − 1.03
Endrin aldehyde	0.76C − 3.86	0.18 $\bar{X}$ +3.91	0.73 $\bar{X}$ − 0.62
Fluoranthene	0.81C+1.10	0.22 $\bar{X}$ +0.73	0.28 $\bar{X}$ − 0.60
Fluorene	0.90C − 0.00	0.12 $\bar{X}$ +0.26	0.13 $\bar{X}$ +0.61
Heptachlor	0.87C − 2.97	0.24 $\bar{X}$ − 0.56	0.50 $\bar{X}$ − 0.23
Heptachlor epoxide	0.92C − 1.87	0.33 $\bar{X}$ − 0.46	0.28 $\bar{X}$ +0.64
Hexachlorobenzene	0.74C+0.66	0.18 $\bar{X}$ − 0.10	0.43 $\bar{X}$ − 0.52

TABLE 7—PRECISION AND RECOVERY AS FUNCTIONS OF CONCENTRATION—METHOD 625 [1]—Continued

Analyte	Recovery, X′ (μg/L)	Single analyst precision, s_r' (μg/L)	Overall precision, S′ (μg/L)
Hexachlorobutadiene	0.71C − 1.01	0.19 $\bar{x}$ +0.92	0.26 $\bar{x}$ +0.49
Hexachloroethane	0.73C − 0.83	0.17 $\bar{x}$ +0.67	0.17 $\bar{x}$ +0.80
Indeno(1,2,3-cd)pyrene	0.78C − 3.10	0.29 $\bar{x}$ +1.46	0.50 $\bar{x}$ +0.44
Isophorone	1.12C+1.41	0.27 $\bar{x}$ +0.77	0.33 $\bar{x}$ +0.26
Naphthalene	0.76C+1.58	0.21 $\bar{x}$ − 0.41	0.30 $\bar{x}$ − 0.68
Nitrobenzene	1.09C − 3.05	0.19 $\bar{x}$ +0.92	0.27 $\bar{x}$ +0.21
N-Nitrosodi-*n*-propylamine	1.12C − 6.22	0.27 $\bar{x}$ +0.68	0.44 $\bar{x}$ +0.47
PCB-1260	0.81C − 10.86	0.35 $\bar{x}$ +3.61	0.43 $\bar{x}$ +1.82
Phenanthrene	0.87C − 0.06	0.12 $\bar{x}$ +0.57	0.15 $\bar{x}$ +0.25
Pyrene	0.84C − 0.16	0.16 $\bar{x}$ +0.06	0.15 $\bar{x}$ +0.31
1,2,4-Trichlorobenzene	0.94C − 0.79	0.15 $\bar{x}$ +0.85	0.21 $\bar{x}$ +0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23 $\bar{x}$ +0.75	0.29 $\bar{x}$ +1.31
2-Chlorophenol	0.78C+0.29	0.18 $\bar{x}$ +1.46	0.28 $\bar{x}$ 0.97
2,4-Dichlorophenol	0.87C+0.13	0.15 $\bar{x}$ +1.25	0.21 $\bar{x}$ +1.28
2,4-Dimethylphenol	0.71C+4.41	0.16 $\bar{x}$ +1.21	0.22 $\bar{x}$ +1.31
2,4-Dinitrophenol	0.81C − 18.04	0.38 $\bar{x}$ +2.36	0.42 $\bar{x}$ +26.29
2-Methyl-4,6-Dinitrophenol	1.04C − 28.04	0.05 $\bar{x}$ +42.29	0.26 $\bar{x}$ +23.10
2-Nitrophenol	1.07C − 1.15	0.16 $\bar{x}$ +1.94	0.27 $\bar{x}$ +2.60
4-Nitrophenol	0.61C − 1.22	0.38 $\bar{x}$ +2.57	0.44 $\bar{x}$ +3.24
Pentachlorophenol	0.93C+1.99	0.24 $\bar{x}$ +3.03	0.30 $\bar{x}$ +4.33
Phenol	0.43C+1.26	0.26 $\bar{x}$ +0.73	0.35 $\bar{x}$ +0.58
2,4,6-Trichlorophenol	0.91C − 0.18	0.16 $\bar{x}$ +2.22	0.22 $\bar{x}$ +1.81

[1] Regressions based on data from Reference 2
X′ = Expected recovery for one or more measurements of a sample containing a concentration of C, in μg/L.
s_r' = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{x}$, in μg/L.
S′ = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in μg/L.
C = True value for the concentration, in μg/L.
$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in μg/L.

TABLE 8—SUGGESTED INTERNAL AND SURROGATE STANDARDS

Base/neutral fraction	Range for surrogate recovery (%) [1]	
	Calibration verification	Recovery from samples
Acenaphthalene-d_8	66–152	33–168
Acenaphthene-d_{10}	71–141	30–180
Aniline-d_5.		
Anthracene-d_{10}	58–171	23–142
Benzo(a)anthracene-d_{12}	28–357	22–329
Benzo(a)pyrene-d_{12}	32–194	32–194
4-Chloroaniline-d_4	1–145	1–145
bis(2-Chloroethyl) ether-d_8	52–194	25–222
Chrysene-d_{12}	23–290	23–290
Decafluorobiphenyl.		
4,4′-Dibromobiphenyl.		
4,4′-Dibromooctafluorobiphenyl.		
1,4-Dichlorobenzene-d_4	65–153	11–245
2,2′-Difluorobiphenyl.		
Dimethyl phthalate-d_6	47–211	1–500
Fluoranthene-d_{10}	47–215	30–187
Fluorene-d_{10}	61–164	38–172
4-Fluoroaniline.		
1-Fluoronaphthalene.		
2-Fluoronaphthalene.		
2-Methylnaphthalene-d_{10}	50–150	50–150
Naphthalene-d_8	71–141	22–192
Nitrobenzene-d_5	46–219	15–314
2,3,4,5,6-Pentafluorobiphenyl.		
Perylene-d_{12}.		
Phenanthrene-d_{10}	67–149	34–168
Pyrene-d_{10}	48–210	28–196
Pyridine-d_5.		
Acid fraction		
2-Chlorophenol-d_4	55–180	33–180
2,4-Dichlorophenol-d_3	64–157	34–182
4,6-Dinitro-2-methylphenol-d_2	56–177	22–307

TABLE 8—SUGGESTED INTERNAL AND SURROGATE STANDARDS—Continued

Base/neutral fraction	Range for surrogate recovery (%) [1]	
	Calibration verification	Recovery from samples
2-Fluorophenol.		
4-Methylphenol-d_8	25–111	25–111
2-Nitrophenol-d_4	61–163	37–163
4-Nitrophenol-d_4	35–287	6–500
Pentafluorophenol.		
2-Perfluoromethylphenol.		
Phenol-d_5	48–208	8–424

[1] Recovery from samples is the wider of the criteria in the CLP SOW for organics or in Method 1625.

TABLE 9A—DFTPP KEY M/Z'S AND ABUNDANCE CRITERIA FOR QUADRUPOLE INSTRUMENTS [1]

m/z	Abundance criteria
51	30–60 percent of m/z 198.
68	Less than 2 percent of m/z 69.
70	Less than 2 percent of m/z 69.
127	40–60 percent of base peak m/z 198.
197	Less than 1 percent of m/z 198.
198	Base peak, 100 percent relative abundance.
199	5–9 percent of m/z 198.
275	10–30 percent of m/z 198.
365	Greater than 1 percent of m/z 198.
441	Present but less than m/z 443.
442	40–100 percent of m/z 198.
443	17–23 percent of m/z 442.

[1] Criteria in these tables are for quadrupole and time-of-flight instruments. Alternative tuning criteria may be used for other instruments, provided method performance is not adversely affected.

TABLE 9B—DFTPP KEY M/Z'S AND ABUNDANCE CRITERIA FOR TIME-OF-FLIGHT INSTRUMENTS [1]

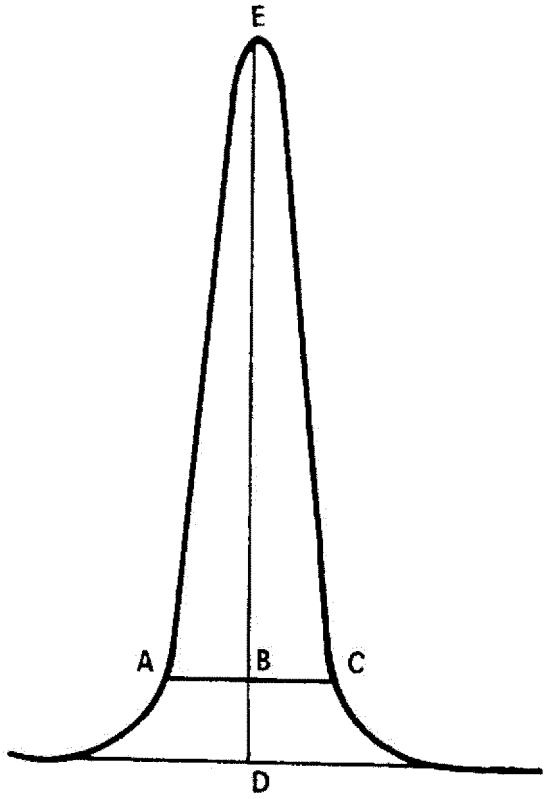
m/z	Abundance criteria
51	10–85 percent of the base peak.
68	Less than 2 percent of m/z 69.
70	Less than 2 percent of m/z 69.
127	10–80 percent of the base peak.
197	Less than 2 percent of Mass 198.
198	Base peak, or greater than 50% of m/z 442.
199	5–9 percent of m/z 198.
275	10–60 percent of the base peak.
365	Greater than 0.5 percent of m/z 198.
441	Less than 150 percent of m/z 443.
442	Base peak or greater than 30 percent of m/z 198.

TABLE 9B—DFTPP KEY M/Z'S AND ABUNDANCE CRITERIA FOR TIME-OF-FLIGHT INSTRUMENTS [1]—Continued

m/z	Abundance criteria
443	15–24 percent of m/z 442.

[1] Criteria in these tables are for quadrupole and time-of-flight instruments. Alternative tuning criteria may be used for other instruments, provided method performance is not adversely affected.

21. Figures



$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

$$\text{Therefore: Tailing Factor} = \frac{12}{11} = 1.1$$

Figure 1 Tailing factor calculation

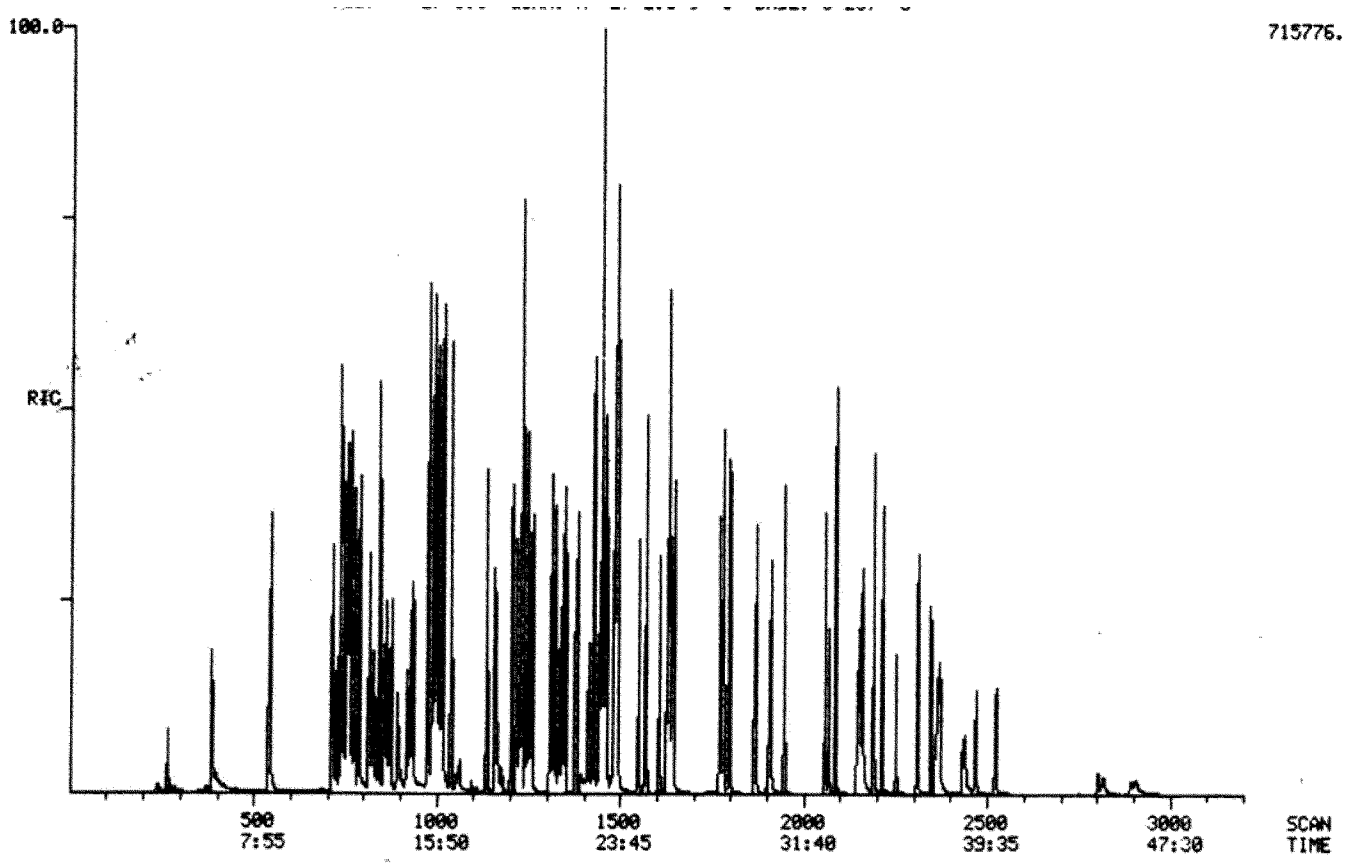


Figure 2 Chromatogram of combined acid/base/neutral standard

BILLING CODE 6560–50–C

22. Glossary

These definitions and purposes are specific to this method but have been conformed to common usage to the extent possible.

22.1 Units of weight and measure and their abbreviations

22.1.1 Symbols

°C degrees Celsius
µg microgram
µL microliter
< less than
> greater than
≤ less than or equal to
% percent

22.1.2 Abbreviations (in alphabetical order)

cm centimeter
g gram
h hour
ID inside diameter
in. inch
L liter
M Molecular ion
m mass or meter
mg milligram
min minute
mL milliliter
mm millimeter
ms millisecond
m/z mass-to-charge ratio
N normal; gram molecular weight of solute divided by hydrogen equivalent of solute, per liter of solution
ng nanogram
pg picogram
ppb part-per-billion
ppm part-per-million
ppt part-per-trillion
psig pounds-per-square inch gauge

22.2 Definitions and acronyms (in alphabetical order)

Analyte—A compound or mixture of compounds (*e.g.,* PCBs) tested for by this method. The analytes are listed in Tables 1–3.

Batch—See Extraction

Blank—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

Calibration—The process of determining the relationship between the output or response of a measuring instrument and the value of an input standard. Historically, EPA has referred to a multi-point calibration as the ''initial calibration,'' to differentiate it from a single-point calibration verification.

Calibration standard—A solution prepared from stock solutions and/or a secondary standards and containing the analytes of interest, surrogates, and internal standards. The calibration standard is used to calibrate the response of the GC/MS instrument against analyte concentration.

Calibration verification standard—The mid-point calibration standard used to verify calibration. See Sections 7.3 and 13.4.

Descriptor—In SIM, the beginning and ending retention times for the RT window, the m/z's sampled in the RT window, and the dwell time at each m/z.

Extracted ion current profile (EICP)—The line described by the signal at a given m/z.

Extraction Batch—A set of up to 20 field samples (not including QC samples) started through the extraction process on a given 12-hour shift (Section 3.1). Each extraction batch must be accompanied by a blank (Section 8.5), a laboratory control

sample (LCS, Section 8.4), and a matrix spike and duplicate (MS/MSD; Section 8.3), resulting in a minimum of five analyses (1 sample, 1 blank, 1 LCS, 1 MS, and 1 MSD) and a maximum of 24 analyses (20 field samples, 1 blank, 1 LCS, 1 MS, and 1 MSD) for the batch. If greater than 20 samples are to be extracted in a 12-hour shift, the samples must be separated into extraction batches of 20 or fewer samples.

Field Duplicates—Two samples collected at the same time and place under identical conditions, and treated identically throughout field and laboratory procedures. Results of analyses the field duplicates provide an estimate of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

Field blank—An aliquot of reagent water or other reference matrix that is placed in a sample container in the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

GC—Gas chromatograph or gas chromatography

Internal standard—A compound added to an extract or standard solution in a known amount and used as a reference for quantitation of the analytes of interest and surrogates. In this method the internal standards are stable isotopically labeled analogs of selected method analytes (Table 8). Also see Internal standard quantitation.

Internal standard quantitation—A means of determining the concentration of an analyte of interest (Tables 1–3) by reference to a compound not expected to be found in a sample.

DOC—Initial demonstration of capability (Section 8.2); four aliquots of reagent water spiked with the analytes of interest and analyzed to establish the ability of the laboratory to generate acceptable precision and recovery. A DOC is performed prior to the first time this method is used and any time the method or instrumentation is modified.

Laboratory Control Sample (LCS; laboratory fortified blank; Section 8.4)—An aliquot of reagent water spiked with known quantities of the analytes of interest and surrogates. The LCS is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

Laboratory fortified sample matrix—See Matrix spike

Laboratory reagent blank—A blank run on laboratory reagents; *e.g.,* methylene chloride (Section 11.1.5).

Matrix spike (MS) and matrix spike duplicate (MSD) (laboratory fortified sample matrix and duplicate)—Two aliquots of an environmental sample to which known quantities of the analytes of interest and surrogates are added in the laboratory. The MS/MSD are prepared and analyzed exactly like a field sample. Their purpose is to quantify any additional bias and imprecision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations.

May—This action, activity, or procedural step is neither required nor prohibited.

May not—This action, activity, or procedural step is prohibited.

Method blank—See blank.

Method detection limit (MDL)—A detection limit determined by the procedure at 40 CFR 136, Appendix B. The MDLs determined by EPA in the original version of the method are listed in Tables 1, 2 and 3. As noted in Sec. 1.5, use the MDLs in Tables 1, 2, and 3 in conjunction with current MDL data from the laboratory actually analyzing samples to assess the sensitivity of this procedure relative to project objectives and regulatory requirements (where applicable).

Minimum level (ML)—The term ''minimum level'' refers to either the sample concentration equivalent to the lowest calibration point in a method or a multiple of the method detection limit (MDL), whichever is higher. Minimum levels may be obtained in several ways: They may be published in a method; they may be based on the lowest acceptable calibration point used by a laboratory; or they may be calculated by multiplying the MDL in a method, or the MDL determined by a laboratory, by a factor of 3. For the purposes of NPDES compliance monitoring, EPA considers the following terms to be synonymous: ''quantitation limit,'' ''reporting limit,'' and ''minimum level.''

MS—Mass spectrometer or mass spectrometry, or matrix spike (a QC sample type).

MSD—Matrix spike duplicate (a QC sample type).

Must—This action, activity, or procedural step is required.

m/z—The ratio of the mass of an ion (m) detected in the mass spectrometer to the charge (z) of that ion.

Preparation blank—See blank.

Quality control check sample (QCS)—See Laboratory Control Sample.

Reagent water—Water demonstrated to be free from the analytes of interest and potentially interfering substances at the MDLs for the analytes in this method.

Regulatory compliance limit (or regulatory concentration limit)—A limit on the concentration or amount of a pollutant or contaminant specified in a nationwide standard, in a permit, or otherwise established by a regulatory/control authority.

Relative retention time (RRT)—The ratio of the retention time of an analyte to the retention time of its associated internal standard. RRT compensates for small changes in the GC temperature program that can affect the absolute retention times of the analyte and internal standard. RRT is a unitless quantity.

Relative standard deviation (RSD)—The standard deviation times 100 divided by the mean. Also termed ''coefficient of variation.''

RF—Response factor. See Section 7.2.2.

RSD—See relative standard deviation.

Safety Data Sheet (SDS)—Written information on a chemical's toxicity, health hazards, physical properties, fire, and reactivity, including storage, spill, and handling precautions that meet the requirements of OSHA, 29 CFR 1910.1200(g) and appendix D to § 1910.1200. United Nations Globally Harmonized System of Classification and Labelling of Chemicals (GHS), third revised edition, United Nations, 2009.

Selected Ion Monitoring (SIM)—An MS technique in which a few m/z's are monitored. When used with gas chromatography, the m/z's monitored are usually changed periodically throughout the chromatographic run, to correlate with the characteristic m/z's of the analytes, surrogates, and internal standards as they elute from the chromatographic column. The technique is often used to increase sensitivity and minimize interferences.

Signal-to-noise ratio (S/N)—The height of the signal as measured from the mean (average) of the noise to the peak maximum divided by the width of the noise.

Should—This action, activity, or procedural step is suggested but not required.

SPE—Solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous solution by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

Stock solution—A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity, authenticity, and concentration of the standard.

Surrogate—A compound unlikely to be found in a sample, and which is spiked into sample in a known amount before extraction or other processing, and is quantitated with the same procedures used to quantify other sample components. The purpose of the surrogate is to monitor method performance with each sample.

* * * * *

■ 9. Revise Appendix B to part 136 to read as follows:

Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 2

Definition

The method detection limit (MDL) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.

Scope and Application

The MDL procedure is designed to be a straightforward technique for estimation of the detection limit for a broad variety of physical and chemical methods. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps used by the laboratory be included in the determination of the method detection limit.

Procedure

(1) Estimate the Initial MDL using one of the following:

(a) The mean plus three times the standard deviation of a set of method blanks.

(b) The concentration value that corresponds to an instrument signal/noise in the range of 3 to 5.

(c) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of spiked blanks.

(d) That region of the standard curve where there is a significant change in sensitivity, *i.e.,* a break in the slope of the standard curve.

(e) Instrumental limitations.

(f) Previously determined MDL.

It is recognized that the experience of the analyst is important to this process. However, the analyst should include some or all of the above considerations in the initial estimate of the MDL.

(2) Determine the Initial MDL

(a) Select a spiking level, typically 2–10 times the estimated MDL in section 1. Spiking levels in excess of 10 times the estimated detection limit may be required for analytes with very poor recovery (*e.g.,* an analyte with 10% recovery, spiked at 100 micrograms/L, mean recovery, 10 micrograms/L; MDL may calculate at 3 micrograms/L. So, in this case the spiking level is 33×MDL, but spiking lower may result in no recovery at all).

(b) Process a minimum of 7 spiked blank samples and 7 method blank samples through all steps of the method, including any sample preservation. Both preparation and analysis of these samples must include at least three batches on three separate calendar dates. Existing data may be used if compliant with the requirements for at least 3 batches and generated within the last 2 years.

(i) If there are multiple instruments that will be assigned the same MDL, then the samples must be distributed across all of the instruments.

(ii) A minimum of two spiked samples and two method blank samples prepared and analyzed on different calendar dates is required for each instrument.

(c) Evaluate the spiking level: If any result for any individual analyte from the spiked blank samples does not meet the method qualitative identification criteria or does not provide a numerical result greater than zero then repeat the spikes at a higher concentration. Qualitative identification criteria are a set of rules or guidelines for establishing the identification or presence of an analyte using a measurement system. Qualitative identification does not ensure that quantitative results for the analyte can be obtained.

(d) Make all computations according to the defined method with final results in the method reporting units.

(i) Calculate the sample standard deviation (S) of the replicate spiked blank measurements and the sample standard deviation of the replicate method blank measurements from all instruments.

(ii) Compute the MDL_s (MDL based on spiked blanks) as follows:

$$MDL_S = t_{(n-1,\ 1-\propto=0.99)}\ S_S$$

Where:

MDL_s = the method detection limit based on spiked blanks

$t_{(n-1,\ 1-\alpha=0.99)}$ = the Student's t-value appropriate for a the single tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom. See Table 1.

S_s = sample standard deviation of the replicate spiked blank sample analyses.

(iii) Compute the MDL_b (MDL based on method blanks) as follows:

(A) If none of the method blanks give numerical results for an individual analyte, the MDL_b does not apply. A numerical result includes both positive and negative results, including results below the current MDL, but not results of ND (not detected) commonly observed when a peak is not present in chromatographic analysis.

(B) If some (but not all) of the method blanks for an individual analyte give numerical results, set the MDL_b equal to the highest method blank result. If more than 100 method blanks are available, set MDL_b to the level that is no less than the 99th percentile of the blank results. For ''n'' method blanks where n ≥ 100, sort the method blanks in rank order. The (n×0.99) ranked method blank result (round to the nearest whole number) is the MDL_b. For example, to find MDL_b from a set of 164 method blanks where the highest ranked method blank results are . . . 1.5, 1.7, 1.9, 5.0, and 10, then 164×0.99 = 162.36 which rounds to the 162nd method blank result. Therefore, MDL_b is 1.9 for n = 164 (10 is the 164th result, 5.0 is the 163rd result, and 1.9 is the 162nd result). Alternatively, you may use spreadsheet algorithms to calculate the 99th percentile to interpolate between the ranks more precisely.

(C) If all of the method blanks for an individual analyte give numerical results, calculate the MDL_b as:

$$MDL_b = \bar{X} + t_{(n-1,\ 1-\propto=0.99)}\ S_b$$

Where:

MDL_b = the MDL based on method blanks

$\bar{X}$ = mean of the method blank results

$t_{(n-1,\ 1-\alpha=0.99)}$ = the Student's t-value appropriate for the single tailed 99th percentile t statistic and a standard deviation estimate with n − 1 degrees of freedom. See Addendum Table 1.

S_b = sample standard deviation of the replicate blank sample analyses.

(e) Set the greater of MDL_s or MDL_b as the initial MDL.

(3) Ongoing Data Collection

(a) During any quarter in which samples are being analyzed, prepare and analyze a minimum of two spiked blanks on each instrument, in separate batches if available, using the same spiking concentration used in Section 2. If any analytes are repeatedly not detected in the quarterly spike sample analysis, this is an indication that the spiking level is not high enough and should be adjusted upward.

(b) Ensure that at least 7 spiked blanks and 7 method blanks are completed for the annual verification.

(c) At least once per year, re-evaluate the spiking level.

(i) If more than 5% of the spiked blanks do not return positive numerical results that meet all method qualitative identification criteria, then the spiking level must be increased and the initial MDL re-determined following the procedure in Section 2.

(d) If the method is altered in a way that can be reasonably expected to change the detection limit, then re-determine the initial MDL according to Section 2, and the ongoing data collection restarted.

(4) Ongoing Annual Verification

(a) At least once per year, re-calculate MDL_s and MDL_b from the collected spiked blank and method blank results using the equations in section 2.

(b) Include data generated within the last 2 years, but only data with the same spiking level.

(c) Include the initial MDL spiked blanks if within two years.

(d) Only use data associated with acceptable calibrations and batch QC. Include all routine data, with the exception of batches that are rejected and the associated samples reanalyzed. If the method has been altered in a way that can be reasonably expected to change the detection limit, use only data collected after the change.

(e) The verified MDL is the greater of the MDL_s or MDL_b. If the verified MDL is within a factor of 3 of the existing MDL, and fewer than 3% of the method blank results (for the individual analyte) have numerical results above the existing MDL, then the existing MDL may optionally be left unchanged. Otherwise, adjust the MDL to the new verification MDL.

Addendum: Determination of the MDL For a Specific Matrix

MDLs may be determined in specific sample matrices as well as in reagent water.

(1) Analyze the sample matrix to determine the native concentration of the analyte(s) of interest.

(2) If the native concentration is at a signal to noise ratio of approximately 5–20, determine the matrix specific MDL according to Section 2, ''Determine the initial MDL'' without spiking additional analyte.

(3) Calculate MDL_b using method blanks, not the sample matrix.

(4) If the signal to noise is less than 5, the analyte(s) should be spiked to obtain a concentration that will give results with a signal to noise of approximately 10–20.

(5) If the analytes(s) of interest have signal to noise greater than approximately 20, then the resulting MDL is likely to be biased high.

TABLE 1—SINGLE TAILED 99TH PERCENTILE T STATISTIC

Number of replicates	Degrees of freedom (n − 1)	$t_{(n-1,\ 0.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
100	100	2.326

Documentation

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. Data and calculations used to establish the MDL must be able to be reconstructed upon request.

The sample matrix used to determine the MDL must also be identified with MDL value. Document the mean spiked and recovered analyte levels with the MDL.

[FR Doc. 2015–02841 Filed 2–18–15; 8:45 am]

BILLING CODE 6560–50–P